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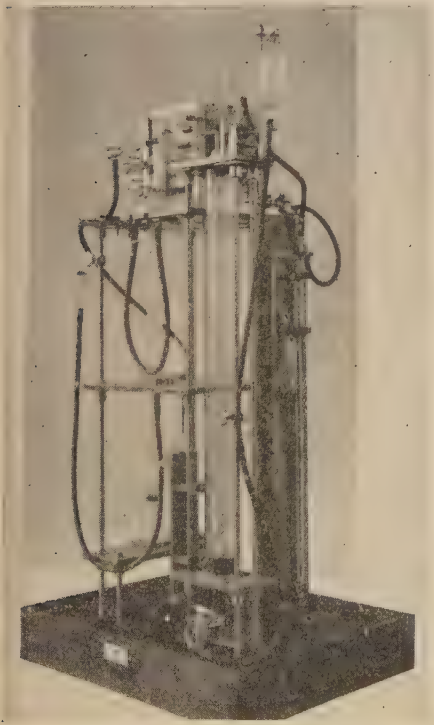

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THE INVESTIGATION OF THE MAGNETIC PROPERTIES OF NON-HOMOGENEOUS SYSTEMS: PART I, EXPERIMENTAL TECHNIQUE

By L. F. BATES, D.Sc., C. J. W. BAKER, B.Sc.
AND R. MEAKIN, B.Sc.,
University College, Nottingham

Received 10 *January* 1940

ABSTRACT. A description is given of a new apparatus and technique for the examination of the magnetic susceptibility of a non-homogeneous material, with particular reference to the investigation of amalgams of metals in dilute solution in mercury. An important feature of the apparatus is that the electromagnet has one pole tip with a cylindrical surface and one pole tip with a plane face, so that when an amalgam is placed in a vertical tube suspended from a torsion balance, each portion of the amalgam is exposed to the same value of the gradient of H^2 in the direction along which motion of the tube is possible; consequently, measurements can be made with amalgams which separate on standing.

§ 1. INTRODUCTION

A SURVEY (1) of the methods which are available for the measurement of the magnetic susceptibilities of solids and liquids shows that in spite of their great variety very few are adequate to deal with non-homogeneous specimens. In fact, it is at once clear that in these cases some modification of the Curie method must be employed. In the normal application of the Curie method, a small body of volume susceptibility k, surrounded by a medium of susceptibility k_a, is placed in a non-uniform magnetic field H so that it is acted upon by a force equal to

$$(k-k_a)vH\frac{dH}{dx} \quad \text{or} \quad \tfrac{1}{2}(k-k_a)v\frac{dH^2}{dx}.$$

Now, these expressions show that to obtain measurable forces and couples with weakly magnetic bodies, fields with pronounced gradients must be used. This means that considerable care must be taken to ensure that different specimens, or their container, etc., are placed and replaced in an accurately determined standard position in the field if satisfactory comparisons are to be obtained. In practice the small body is placed in the region where $H\,dH/dx$ is a maximum, but, in order to lessen errors due to inexact placing of the specimen, the maximum is usually made to be a flat one and the body used is as small as possible. Fereday (2) proved that by using an electromagnet with special pole tips of different sizes, one convex and one concave, with different radii of curvature of the spherical faces, it is possible to make $H\,dH/dx$ constant over a distance as great as 1 cm. While this represents an important advance in experimental technique over earlier work, it should be pointed out that with spherical pole tips $H\,dH/dx$ can be made constant in one direction only, so that the method is not applicable to non-homogeneous specimens unless very small specimens are used.

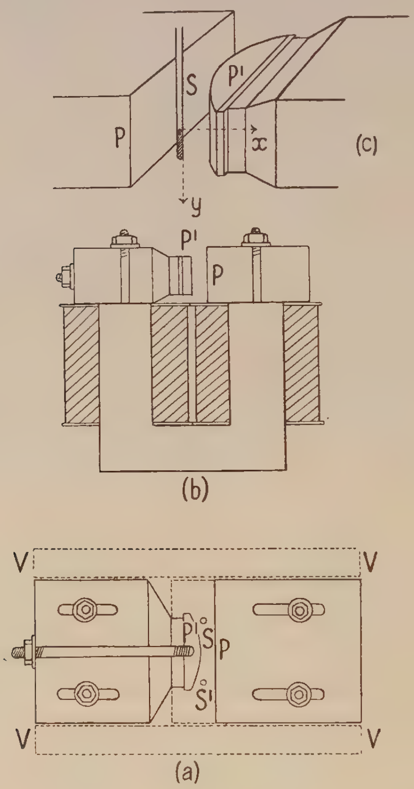


Figure 1. Magnet showing pole tips and positions of specimen and blank tubes. (*a*) Plan. (*b*) Front elevation. (*c*) Back view of pole tips to illustrate forces.

In recent years an intensive study (3) of the magnetic properties of amalgams has been made in this laboratory. In many of the experiments the Gouy method was used under conditions which were thought to be entirely satisfactory, but cases arose where the use of the method appeared to be dangerous. For example, while an investigation of silver amalgams by this method was made with a little difficulty, the corresponding investigation of gold amalgams was impossible; for in the latter case a component rich in gold sank to the bottom of the container and all attempts to form a homogeneous amalgam failed. Now, if the Curie method were employed in its usual form with gold amalgams, the results would undoubtedly be useless; if the modification of Fereday were used, the quantity of amalgam required would be so small that the specimens containing known small quantities of gold, which are of theoretical interest to us, could not be prepared with certainty of composition.

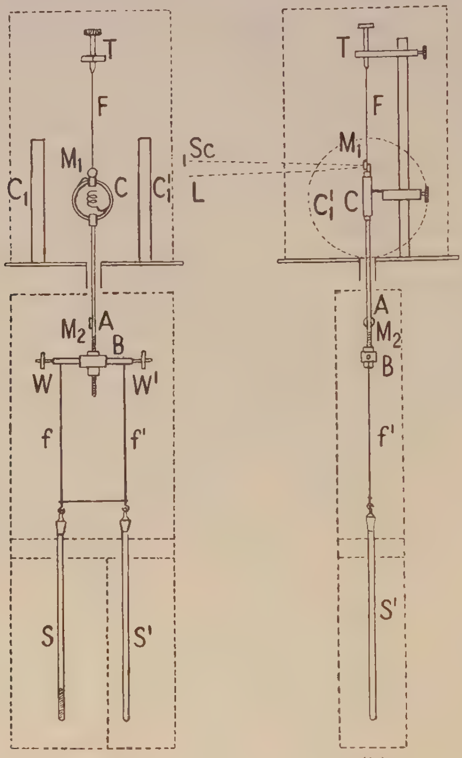
A new modification of the Curie method has therefore been devised in which the spherical pole tips of the Fereday type have been replaced by pole tips with plane and cylindrical surfaces respectively. If we refer to figure 1, (*a*) represents the plan and (*b*) the side view of a magnet of the type designed by Rutherford for radioactivity measurements, and adapted for present purposes. P represents the pole tip with a plane surface and P′ that with a cylindrical face. P is 16·5 cm. long and 10 cm. deep, while P′ is 6·0 cm. deep, the radius of curvature being 7·0 cm. If, therefore, a tube is placed in a position such as that shown diagrammatically in figure 1 (*c*) and indicated by S and S′ in figure 1 (*a*), then by suitable adjustment of the distance apart of P and P′, the lower ends of the tube S can be made to occupy a region in which $H\, dH/dx$ is constant over a reasonable distance along x and independent of the depth of the bottom of the tube below the horizontal plane containing the centres of the pole tips. Hence, when the tube is thus placed, the magnetic forces upon any small element of volume of a specimen placed in the tube must be independent of the position occupied by that element. Consequently, in the case of a non-homogeneous specimen, the precise distribution of its constituents in the tube is of no importance, as far as the magnetic forces are concerned. It is therefore clear that an amalgam which separates on standing can be investigated with this system. In the light of this introduction, we may consider the nature of the magnetic forces in the general case, but before doing so it is helpful to consider first the actual experimental arrangements by which they are measured.

§ 2. DESCRIPTION OF APPARATUS AND METHOD

The general form of the apparatus is shown in figure 2, certain features of the depicted arrangements being necessary because the magnet had rather an extensive stray field.

The specimen tube S in which the amalgam was placed was suspended on a copper frame f f′ attached to an aluminium cross-bar. A similar but evacuated tube S′ was suspended from the other side of f f′ and the bronze weights WW′ were used to make the cross-bar horizontal. The latter was attached by a brass rod A to the lower surface of a coil C which was suspended by the metal suspension F from the torsion head T. The suspension was made of the alloy B.O. 181 supplied by Messrs. Johnson and Matthey, and we are much indebted to Dr. H. Shaw of the Science Museum for recommending the use of this excellent material; it was about 8·5 cm. long and 0·05 mm. diameter and its torsion constant was very low and remarkably constant. The coil C was 2·2 cm. in diameter and consisted of 20 turns of enamelled copper wire cemented together; it formed the movable coil of an electrodynamometer system of which C_1 and C_1' were the fixed coils. These were each of 100 turns and 9·5 cm. in mean diameter and were wound on ebonite formers. Owing to the large stray field of the magnet alternating current had to be used to work the electrodynamometer.

Let the tube S contain a small quantity of mercury, and suppose that when the magnet is not excited a current i_0' is passed through the electrodynamometer so that S and S′ are brought to standard positions with respect to P and P′. The mirror M_1 then reflects an image of a cross-wire on to the zero of the scale Sc, figure 2 (*b*), and the position of the image is viewed through a telescope. On exciting the magnet the tube S is repelled more than the tube S′ from the face P′, but the system can be brought back by the passage of a current i_1' through the electrodynamometer, measured by a special method detailed below. The electrodynamometer system was mounted on a substantial wooden framework which was supported partly from a slate slab and partly from the heavy base of the magnet. As it was necessary to deal both with paramagnetic and diamagnetic specimens the switch K_2 was employed to reverse the connections to the suspended coil, thus reversing the direction of the restoring couple.



(a) (b)

Figure 2. (*a*) Front view, (*b*) side view of electrodynamometer and tube system.

The design of the tubes S and S′ is shown in figure 3 (*a*). Each consisted of a pyrex tube about 21 cm. long and about 0·35 cm. internal diameter, provided with a ground-glass stopper which was used to hook the tube to the framework f f′, after the tube had been evacuated by a Hyvac pump. For this purpose the special device shown in figure 3 (*b*) was used. Two tubes t_1 and t_2 were sealed into the sides of a short but wide piece of glass tube X X′; t_1 was connected through a drying tube to the Hyvac pump, while t_2 was connected to a small bulb B, of which the use will be described later. Over the end X′ was slipped a piece of rubber pressure-tubing. The bore of the latter tubing was very important, for the specimen tube S, when lightly lubricated with glycerine, had to slide through the tubing so that with gentle forcing it could readily be manipulated into the position shown in figure 3 (*b*). Over the end X a short length of rubber gas-tubing was next placed as shown and provided with a screw pinchcock P_1. On closing P_1, withdrawing the stopper of S by gripping it through the soft gas-tubing, and switching on the Hyvac pump, the tube S could be evacuated. On completion of the evacuation the stopper could again be gripped and pushed into the mouth of the tube, so that on opening P_1 the stopper was forced into position by the pressure of the atmosphere; this was sufficient to keep it fixed and to support the weight of the tube and its contents when the tube was suspended from the hook. The tubes were then removed from the pressure tubing, the traces of glycerine were washed off and the stopper was turned to occupy a standard position as shown by fiducial marks on the stopper and tube. The tube was always attached in a standard

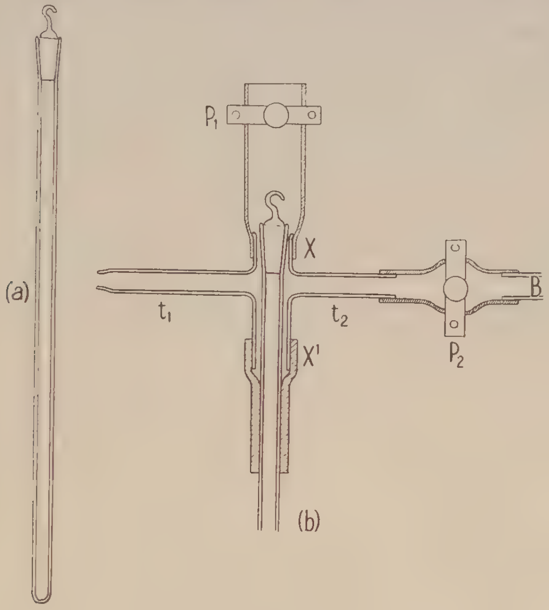


Figure 3. (*a*) Specimen tube and (*b*) evacuation apparatus.

way to f f′ and the values of the restoring currents for chosen field-currents in the electromagnet were measured several times after repeated removal and replacement of S to ensure that it occupied its proper position between the pole tips. The electrodynamometer was enclosed in a wooden case, while the lower part of the moving system was enclosed in a brass box, shown by the broken lines in figure 2, and the upper part by a wooden box which fitted on to the brass one. A series of paper baffles served to prevent convection currents in the boxes.

§ 3. MEASUREMENT OF RESTORING COUPLES

From the theory of the method it is clear that the measure of magnetic forces acting upon the specimen is provided by the difference of the squares of the two currents supplied to the electrodynamometer. Consequently, if an accuracy of 1 part in 1000 is desired, this difference must be known to at least this degree, which means that the individual currents must be known to an accuracy of 5 parts in 10,000. The electrical connections are shown in figure 4 and they form three circuits *a*, *b* and *c*. Circuit *a* supplies current from the A.C. mains to the electrodynamometer through a set of adjustable resistances and a 180 ma.-thermojunction placed in series with a thermogalvanometer T.G. supplied by the Cambridge Instrument Company. When an extra resistance was connected in series with the thermogalvanometer this was found very satisfactory for preliminary measurements of the electrodynamometer current, the thermal scale being read directly. It was made much more useful for the work in hand, as follows:—

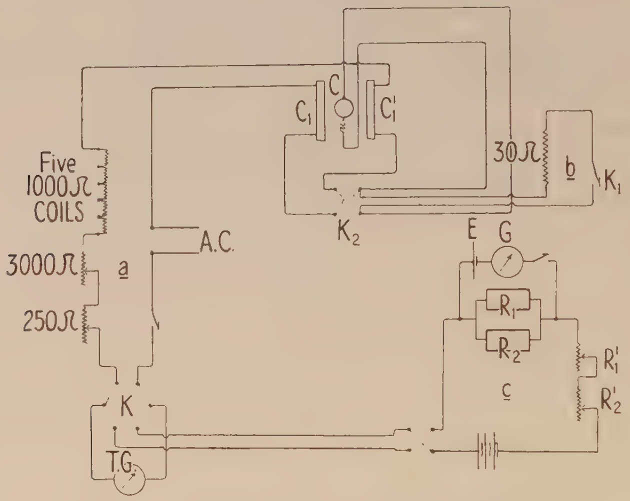


Figure 4. Circuit diagram for electrodynamometer.

The value of the current on the thermal scale was not read directly from the pointer, but the latter was viewed through a telemicroscope with a fine scale in the eye-piece. The telemicroscope was adjusted in a suitable position and clamped rigidly, the position of the pointer image on the eye-piece scale being noted when the A.C. current applied brought the image of the cross-wire to the zero on the scale Sc., figure 2 (*b*). In practice the electrodynamometer system was not brought to rest but the image was allowed to move between small limits on the scale and its actual position of rest was calculated. In order to control the motion of the system effectively the damping circuit was used. By closing the key K_1 the electrodynamometer coil was shorted by a resistance of 30 ohms, so that by systematic opening and closing of K_1 the amplitude of the system could be quickly reduced.

By operating the switch K the thermogalvanometer could be placed in series with a battery of accumulators and the resistances shown in the potentiometer circuit *c* of figure 4. The image of the pointer of the thermogalvanometer was brought to the exact position in the eye-piece scale which it formerly occupied when the A.C. current was passing through the instrument, by adjustment of the resistances in the circuit *c*. The Weston standard cell E was then balanced against the potential drop across the resistances R_1 and R_2 in parallel, the total resistance of the battery circuit being, of course, kept constant. R_1 was provided by a first-class dial resistance box with a range 1 to 111 ohms and R_2 by a similar box with a range 1 to 11, 110 ohms. As the value of the resistance R_1 usually lay between 20 and 30 ohms and the resistance R_2 was some thousands of ohms, a very satisfactory fine adjustment of the balancing potential was possible. The current necessary was thus equal to $1{\cdot}0183\,(1/R_1+1/R_2)$ amp. This arrangement worked excellently and we experienced no trouble with the thermojunction circuit; the junction and the resistance terminals, etc. were, of course, heavily lagged with cotton wool.

§ 4. THEORY OF THE METHOD

The discussion of the method is facilitated if we assume that the tube S is placed in a field very similar to that in which S′ is placed and that S′ merely acts as a kind of magnetic counterpoise or "dummy". We may therefore leave it out of account in making our calculations. If we suppose that in figure 1 (*c*) we start with the evacuated tube S containing pure mercury to a chosen height, we may write

$$\Gamma i_0^2 - C\theta = k_0 v H \frac{dH}{dx} + E \qquad \ldots\ldots(1),$$

where i_0 is the current supplied to the electrodynamometer, Γ is the constant of the instrument, $C\theta$ is a term representing the twist in the fibre produced by bringing S to its standard position, E is the couple which would be exerted on the empty tube, v is the volume of the mercury and k_0 its volume susceptibility.

If the mercury is now removed and S is again evacuated, we have for the condition of equilibrium for the empty tube in the standard position,

$$\Gamma i_e^2 - C\theta = E \qquad \ldots\ldots(2),$$

where i_e is the current now supplied to the electrodynamometer. Subtracting (2) from (1) we have

$$\Gamma(i_0^2-i_e^2)=k_0 v H\frac{dH}{dx}=m_0\chi_0 . H\frac{dH}{dx} \qquad \ldots\ldots(3),$$

where m_0 is the mass of the mercury used and χ_0 the mass susceptibility of pure mercury. If we now place a mass m of amalgam of susceptibility χ in the tube we have, in like manner,

$$\Gamma(i^2-i_e^2)=m\chi H\frac{dH}{dx} \qquad \ldots\ldots(4),$$

where i is the current supplied to the electrodynamometer when the amalgam is *in situ*. Hence

$$\chi=\frac{m_0}{m}\chi_0\frac{(i^2-i_e^2)}{(i_0^2-i_e^2)} \qquad \ldots\ldots(5).$$

On this theory the evaluation of χ requires the knowledge of two masses m and m_0, and the measurement of three different electrodynamometer currents.

Now, the derivation of equation (5) is based on the following assumptions:—

(*a*) $H\,dH/dx$ remains constant during the whole of the measurements ;
(*b*) a slight error in the replacement of the tube S is unimportant ;
(*c*) the height of mercury or amalgam in the tube is immaterial ;
(*d*) the constituents of the amalgam may be distributed in any manner throughout its mass ;
(*e*) no ferromagnetic impurity is present in the materials used.

Condition (*a*) is usually satisfied when the magnet is used under carefully controlled conditions of temperature and current. For this reason the heavy pole-pieces were kept at a constant temperature by passing water through the closed rectangular copper vessels V V indicated by the dotted lines in figure 1. Moreover, a separate tube similar to S and containing mercury was kept as a standard and was periodically inserted in place of S; the value of the electrodynamometer current then showed at once whether the field had changed. The water-cooled vessels also served to maintain the temperature of the air in the brass box at a constant value so that the susceptibility of the air, and hence E, also remained constant throughout.

Condition (*b*) means that over a restricted range the results obtained should be independent of the initial choice of zero and that, if we could picture such an extreme example, the results obtained with an amalgam should be independent of any lateral unevenness in the distribution of the amalgam constituents in the tube. We satisfied ourselves that this condition obtained in the following way:—

A chosen current was supplied to the electromagnet, and the tube S containing pure mercury was brought to a series of definite positions as recorded by the image of the cross-wires on the scale Sc. The mean square of the electrodynamometer current, obtained directly from the reading on the thermal scale of the thermogalvanometer, was plotted as a function of the reading on Sc. This was therefore equivalent to plotting the restoring couple acting on S as a function of the latter's position, for, if i_0 and i'_0 represent the electrodynamometer currents for the positions θ and θ', we have from equation (1)

$$\Gamma i_0^2 - C\theta = m_0\chi_0\left(H\frac{dH}{dx}\right)+E$$

and

$$\Gamma i'^2_0 - C\theta' = m_0\chi_0\left(H\frac{dH}{dx}\right)'+E,$$

so that

$$\Gamma(i_0^2 - i'^2_0) = C(\theta-\theta') \qquad \ldots\ldots(6)$$

if $H\,dH/dx$ and E are both independent of position. At first sight it would seem that E is a very important quantity, but it must be remembered that the presence of the "dummy" tube S′ is responsible for a couple which is oppositely directed to that on the walls of S, so that in effect E is small, and the main control on the system when S and S′ are both empty is provided by the suspension. Consequently, on plotting $(i_0^2 - i'^2_0)$ as a function of θ', we get a straight line if $H\,dH/dx$ is constant. As the tube S is really mounted on the arm of a torsion balance, it is actually displaced along a curved path, but this is quite short and we may treat it as straight. The results for three several values of the field current are shown in curves (1), (2) and (3) of figure 5. The curves (1) and (2) intersect on the axis, provided we neglect the lowest readings, and, accordingly, it was decided to use a constant field-current of 6 amperes and to work with a fixed zero corresponding to a reading of 15 cm. on the scale. Now a displacement of the image of the cross-wires of 1 cm. corresponded to a lateral movement of the tube S through 0·025 mm.; as it was easily possible to sight the position of the image on Sc with an accuracy of 0·25 mm., this means that the tube could be restored to the standard position to within less than 0·006 mm. Of course, the tube S must be hooked

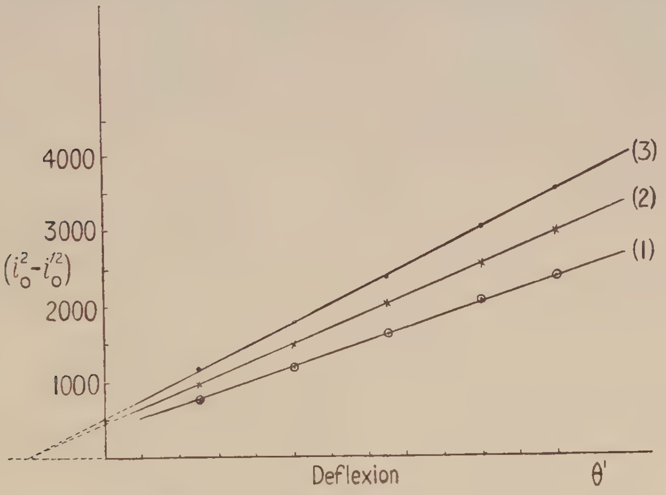


Figure 5. Curve of deflexion θ' with restoring couple $(i_0^2 - i'^2_0)$, in arbitrary units, for currents of (1) 4 amp., (2) 6 amp. and (3) 8 amp. in magnet coils.

on to the cross-bar in a standard manner. Fortunately this can be checked readily by means of the light reflected from the mirror M_2, which must always form an image of a cross-wire upon a fixed mark on the wall near the apparatus.

We now come to the condition (*c*), which is of the greatest importance, because, unless the position which a given mass of mercury occupies inside the tube S is immaterial within reasonable limits, the arrangement is useless. Luckily this can easily be tested, since from equation (3) the quantity $(i_0^2-i_e^2)$ should be directly proportional to the mass of mercury used. In checking that the condition is satisfied, one preliminary adjustment is necessary; the tube S containing a little mercury must be adjusted to hang with its lower end in a suitable region in the field. For example, if the tube hangs too low, some of the mercury will be in a very unsatisfactory position. The adjustment can be done quickly by trial; in any case, we shall see that we have an easy method of checking that it has been correctly done. In figure 6 are given the results of a series of measurements of the couple acting on given masses of mercury in the tube S. We see that the initial portion of the graph is linear and passes through the origin. Hence the lower end of the tube is in a suitable portion of the field. The linear portion of the graph extends to a mass of mercury which fills the tube to a height of 3·3 cm., but masses greater than 5 gm. are acted upon by forces arising from the very non-uniform fields at the edges of the gap.

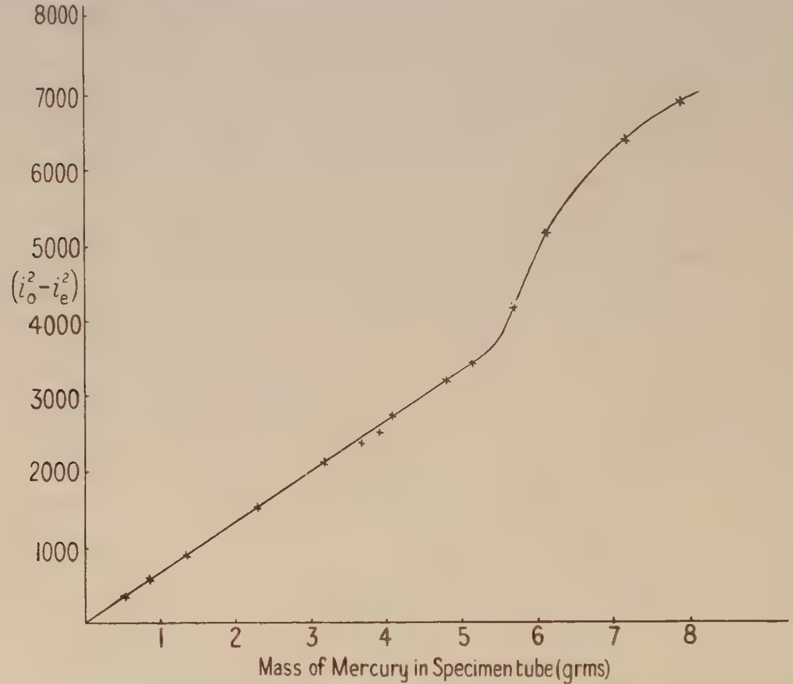


Figure 6. Relation between restoring couple in arbitrary units and mass of specimen.

The readings for masses in the neighbourhood of 3·7 gm. are a little erratic, but it is seen from figure 1 that the pole tip P′ is fixed by a screw, and there must be some non-uniformity in the magnetization of the iron in its neighbourhood. Therefore, in our experiments we always worked with masses of mercury between 4·25 and 4·4 gm. and with our amalgams of such concentrations that any light components which floated to the top of the fluid were outside the region of non-linear relation of force to added mass. Hence, in satisfying conditions (*b*) and (*c*), condition (*d*) was also fulfilled.

We are thus left with the final condition (*e*). In the above theory the materials are assumed to be free from ferromagnetic impurity. In practice mercury can be readily obtained pure and the presence of one part in a million of ferromagnetic impurity in an amalgam is easily detectable, and at first sight it would appear possible to devise at least three different ways of eliminating the effects of ferromagnetic impurity. We tested such possibilities using either ferromagnetic amalgams of known iron content or short copper rods inside S, the copper containing slight traces of ferromagnetic impurity whose saturation intensity of magnetization was known from other experiments. We were forced to conclude that with the above arrangement there is no satisfactory way of allowing for ferromagnetic impurity; it is imperative that none should be present in precision measurements.

ACKNOWLEDGEMENTS

Much of the apparatus was purchased by a grant to one of us (L. F. B.) by the Government Grant Committee of the Royal Society.

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THE INVESTIGATION OF THE MAGNETIC PROPERTIES OF NON-HOMOGENEOUS SYSTEMS: PART II, THE MAGNETIC PROPERTIES OF NICKEL AMALGAMS

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ABSTRACT. The apparatus described in Part I* is used to measure the magnetic susceptibilities of a series of nickel amalgams containing 0·01 to 2·68 per cent of nickel by weight over the temperature range 15° to 300° c. All freshly prepared amalgams which have not previously been heated are diamagnetic, the nickel exhibiting a paramagnetic mass-susceptibility which is approximately independent of temperature. When an amalgam is heated to 225° c. it becomes ferromagnetic, and the ferromagnetism persists when the amalgam is cooled. The results are explained in terms of some new views on the ferromagnetism of nickel recently put forward by Néel.

§ 1. EXPERIMENTAL PROCEDURE

When the apparatus described in Part I was designed it was not contemplated that it would immediately be used with amalgams of a ferromagnetic with mercury, but in the course of other work in this laboratory it was found that nickel amalgams showed no trace of ferromagnetism, and they were used in the first investigation. The amalgams were prepared by the electrolytic denudation of nickel sulphate solutions containing known quantities of nickel, using as cathode a weighed quantity of mercury which was sufficient to fill the tube S to the extent indicated in the discussion of condition (*d*), Part I. Each freshly prepared amalgam was quickly washed with distilled water, roughly dried and placed in S, which was then evacuated as described with reference to figure 3 of Part I, the lower end of S being placed in a bath of hot water at frequent intervals during the evacuation in order to drive off all water from the amalgam. It was then ready for examination, and, as a recent investigation of the electrical properties of nickel amalgams had shown that very interesting changes in resistivity occur at about 220° c., it was decided to make experiments up to that temperature. The lower end of the tube S was therefore surrounded by a narrow cylindrical furnace consisting of a copper tube coated with asbestos paper and purimachos cement on which "glowray" wire was wound non-inductively as heating element.

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* This volume, p. 425.

This was in turn coated with purimachos and slipped inside the inner tube of a water jacket. The furnace was mounted on a Sindanyo base and heated by alternating current. The temperature of S and its contents was recorded by a copper *vs.* constantan thermojunction placed immediately below, and almost in contact with, the lower end of S.

Now, when mercury was heated in the evacuated tube S, the surface of the fluid naturally became disturbed at high temperatures and the readings of the currents supplied to the electrodynamometer became unreliable. It was found necessary to place an inert gas above the fluid, and for this purpose the bulb B was attached to the side tube t_2 shown in figure 3 of Part I. In it was placed a small quantity of solid carbon dioxide. Before attaching B and opening P_2, the stopper was placed in S. B was then attached and P_2 was opened, the carbon dioxide being pumped off until all the air was removed from the apparatus. The stopper of S was thereupon slipped out, the pump was stopped and the pressure of the carbon dioxide was allowed to rise until it reached 20 cm. of mercury at room temperature, when the stopper was replaced in S. This pressure, while enough to prevent surface disturbances in the mercury, did not increase sufficiently with rise in temperature to expel the stopper from S.

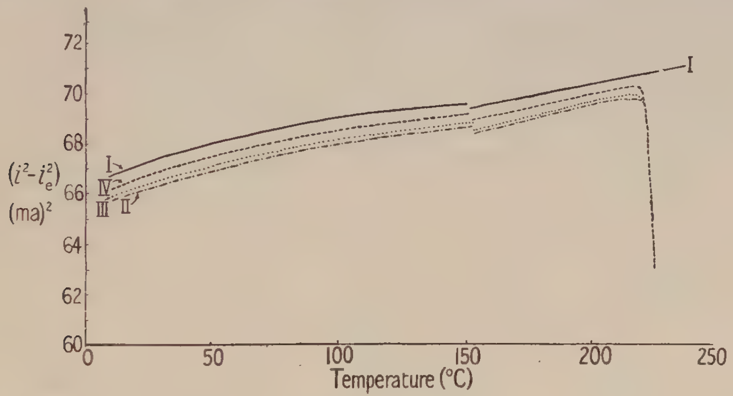

Figure 1. Graph of electrodynamometer couple, proportional to $(i^2-i_e^2)$, against temperature for a series of amalgams of stated concentrations.

I. Pure Hg
II. 0·00987 % Ni
III. 0·0196 % Ni
IV. 0·0382 % Ni

The quantities of mercury used in the determination of the several curves are different.

Carbon dioxide gas has the advantage that it is so weakly diamagnetic that no allowance for its magnetic properties need be made in the calculations. Its use, however, entails one unfortunate disadvantage, which is probably not peculiar to carbon dioxide gas, in that it produces a definite change in the magnetic properties of mercury. Certain discrepancies in the variation of the magnetic behaviour of different samples of mercury with temperature were recently proved to arise unless the mercury was carefully degassed, a kind of discontinuity appearing in the $\{\chi, T\}$ curves in the neighbourhood of 150° c. when the mercury was not degassed. This showed quite clearly in the measurements of Bates and Baker by the Gouy method, and such discontinuities are even more pronounced in the work described here. Indeed, a comparison of figure 1 in the original paper by Bates and Baker(1) with the curves for pure mercury in figures 1 and 2 of this paper shows how much more sensitive is the newer method of investigation. It may also be mentioned that in the newer method the properties of the whole of the mercury specimen are measured, whereas, in the Gouy method, that portion of the mercury within the uniform field plays practically no part and the magnetic properties measured are those of the portion which happens to be in the region near the edge of the pole pieces, where $H\,dH/dx$ is a maximum.

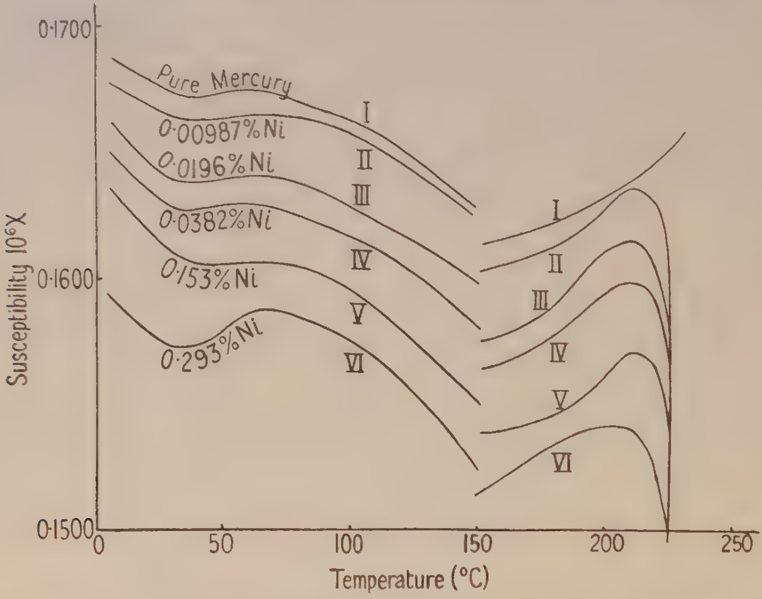

Figure 2. Variation with temperature of susceptibility of nickel amalgams of stated concentrations.

§ 2. RESULTS

The theory of the relevant measurements has been fully described in Part I; in order to give an idea of the precision of the method for a few of the amalgams investigated, the values of $i^2 - i_c^2$ are plotted against the corresponding temperatures in figure 1. Here the discontinuity mentioned above is clearly manifest in the case of each amalgam. The data of table 1 and the representative curves of figure 2 are obtained by taking the necessary values of i^2 at chosen temperatures from curves such as those of figure 1. The results for the weakest amalgam in table 1 are not regarded as entirely reliable, as difficulty was experienced in dealing adequately with such a small quantity of nickel. The curve for "pure" mercury is obtained on the basis that the mass susceptibility of pure mercury at 20° c. is 0·1680 e.m.u. per gm.; the inverted commas are used as a reminder that the mercury is confined in the presence of gas. All the values in this paper are therefore standardized with reference to the value assumed for pure mercury.

Referring to table 1 it is seen that if for a chosen temperature we plot the susceptibilities of amalgams of different concentrations against the concentration of nickel, the paramagnetism at first increases rapidly with increase in nickel content and then reaches a more or less steady condition in which the paramagnetism rises but slightly. With concentrations greater than 1·2 per cent of nickel the paramagnetism again shows a marked rate of increase with concentration.

Table 1. Mass susceptibilities of nickel amalgams

Temp. °c.	Concentration of nickel, per cent by weight								
	"Pure" Hg	0·00987	0·0196	0·0382	0·153	0·293	1·240	1·925	2·68
10	·1685	·1675	·1658	·1646	·1631	·1588	·1563	·1512	·1414
20	·1680	·1669	·1648	·1636	·1620	·1579	·1555	·1498	·1408
30	·1674	·1664	·1639	·1628	·1610	·1573	·1551	·1488	·1403
50	·1674	·1663	·1639	·1629	·1606	·1579	·1560	·1497	·1404
70	·1674	·1665	·1640	·1629	·1606	·1588	·1569	·1507	·1404
90	·1666	·1662	·1634	·1620	·1601	·1580	·1581	·1508	·1404
110	·1661	·1652	·1622	·1612	·1591	·1568	·1585	·1512	·1418
130	·1644	·1639	·1612	·1598	·1570	·1551	·1581	·1501	·1426
150	·1628	·1624	·1598	·1581	·1552	·1524	·1566	·1493	·1448
160	·1615	·1605	·1577	·1566	·1539	·1515	·1539	·1474	·1431
180	·1621	·1612	·1588	·1577	·1545	·1533	·1512	·1483	·1438
200	·1632	·1626	·1610	·1593	·1561	·1535	·1508	·1432	·1424
210	·1639	·1635	·1614	·1598	·1570	·1540	·1536	·1430	·1416
220	·1644	·1629	·1604	·1591	·1564	·1520	·1404	·1341	—

From the data in table 1 we may obtain an estimate of the susceptibility possessed by the nickel which goes into solution in a weak amalgam. Thus, if we take the amalgam with concentration 0·00987 per cent nickel we may write

$$(100{\cdot}00987)(-0{\cdot}1669)10^{-6} = (100)(-0{\cdot}1680)10^{-6} + 0{\cdot}00987\chi_{\mathrm{Ni}},$$

whence
$$\chi_{\mathrm{Ni}} = \frac{0{\cdot}110}{0{\cdot}00987} \times 10^{-6}$$
$$= 11{\cdot}1 \times 10^{-6} \text{ e.m.u. per gm. at } 20^\circ \text{ c.}$$

In this way we may obtain the mass susceptibility of the nickel in dilute solution at different temperatures. The values based on the amalgam of concentration 0·0382 per cent nickel are given in table 2.

Table 2. Mass susceptibility of nickel in dilute solution at stated temperatures

T° c.	10	20	30	50	70	90	110
$10^6\chi_{\mathrm{Ni}}$	10·2	11·5	12·1	11·8	11·8	12·1	12·8
T° c.	130	150	160	180	200	210	220
$10^6\chi_{\mathrm{Ni}}$	12·1	12·3	12·8	11·5	10·2	10·7	13·9

This means that over a wide range of temperature the nickel has a fairly constant paramagnetism, which, within the limits of experimental error, is about 700×10^{-6} c.g.s. units per gm. atom.

It is of interest to follow the behaviour of one of the weaker amalgams after it has been heated to about 224° c. For this purpose the switch K_2 was used to reverse the direction of the current in the coil C with respect to that in the coils C_1 and C_1'. A set of measurements is reproduced in figure 3. The dots refer to readings obtained while the amalgam was being heated for the first time and the encircled points to those obtained when heated for a second time. As we have pointed out in Part I, the apparatus is not suitable for the accurate investigation of ferromagnetics, but it is safe to deduce from figure 3 that on subsequent heating a pronounced decrease in ferromagnetism occurs between room temperature and 220°, and that this is succeeded by a rapid increase in ferromagnetism over a restricted range of temperature, to be followed by a decrease in ferromagnetism up to the maximum temperature which can be reached in these experiments.

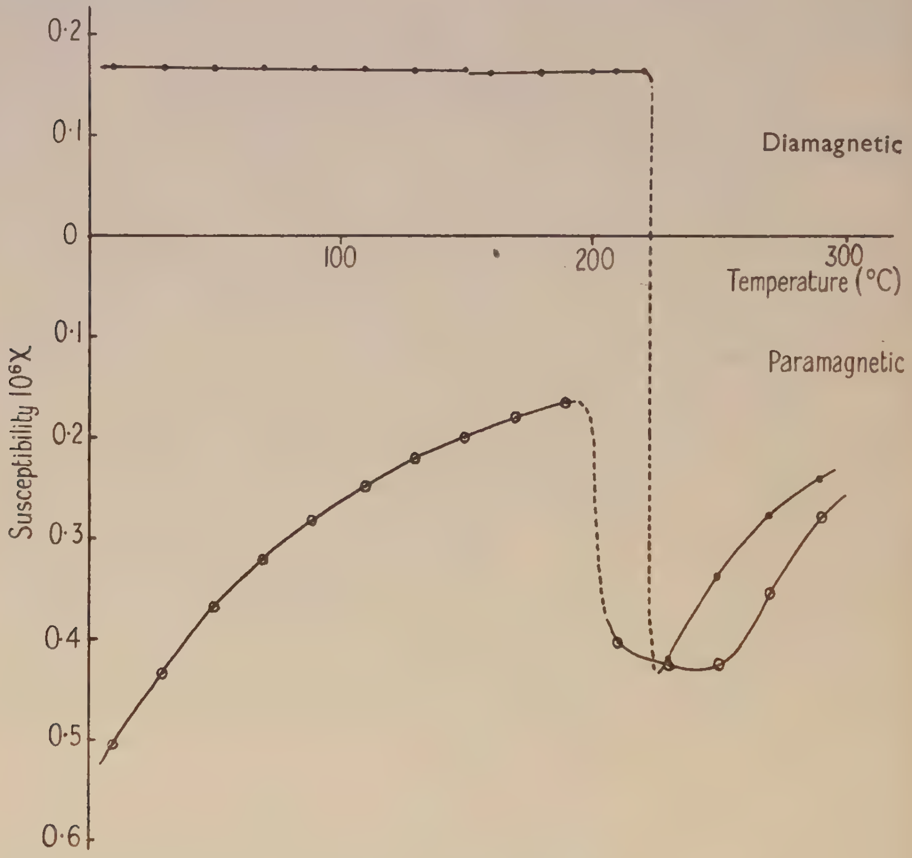

Figure 3. Behaviour of a nickel amalgam on initial and subsequent heating.

§ 3. DISCUSSION

The results obtained above may best be discussed in the light of some new views on the ferromagnetism of nickel which have recently been put forward by Néel⁽²⁾. Néel postulates that a transition metal consists of a mixture of ions, i.e. atoms surrounded by their $3d$ electrons and immersed in an atmosphere of $4s$ electrons. In the case of nickel he adduces evidence to show that in the bulk metal one ion is a neutral $3d^{10}$ ion possessing zero magnetic moment, while the other is a $3d^9$, or even a $3d^8$ ion, which is a magnetic carrier. An equilibrium exists between the two types, which can be influenced by the addition of metals with spare s electrons. Thus, if we dissolve a nickel atom in a metal in which the number of s electrons is greater than 0·6 per atom, then the nickel will tend to form $3d^{10}$ ions. This is precisely what happens when nickel is dissolved in the monovalent metals copper, silver or gold, when it acquires a paramagnetism independent of temperature.

It has been shown above that nickel in freshly prepared dilute solution in mercury also exhibits a paramagnetism more or less independent of the temperature over a wide range. At the same time the atomic paramagnetism is very large, like that of chromium and of manganese. In these substances it is suggested that electron spins are oppositely directed, under the influence of a negative internal field, so that the substances may be termed antiferromagnetic⁽³⁾, but an external field disturbs the arrangement of spins and causes the metals to acquire temporary magnetic moments which are independent of temperature. Again, Bates and Prentice⁽³⁾ showed that the conductivity of a nickel amalgam is greater than that of pure mercury, and that there is a sudden change when the amalgam becomes ferromagnetic. This is in keeping with the view that in place of $3d^{10}$ ions some $3d^9$ or $3d^8$ ions are now present, so that the electrical resistance is increased, corresponding to the passage of conductivity electrons from the s band to holes in the d band.

Now, the onset of ferromagnetism with rise in temperature, as shown in figures 1 and 2, is very sudden and much more marked than the corresponding change in conductivity. This can be readily explained if we are dealing with an ionization process, for (as a basis for discussion) we may consider that the number of $3d^9$ ions at any temperature is proportional to $T^2e^{-b/T}$, where b is a constant. The latter expression would account for the fairly sharp change in conductivity with temperature which is observed. However, for ferromagnetism to appear, each atom of the ferromagnetic must be surrounded by at least eight neighbours, so that the number of ferromagnetic clusters or groups of atoms may be considered proportional to the eighth, if not a higher, power of $T^2e^{-b/T}$, and this would account for the very sharp change in magnetic properties of the amalgams which is in fact observed. We may therefore conclude that these experiments provide very striking evidence in support of Néel's views.

ACKNOWLEDGEMENT

Much of the apparatus was purchased by a grant to one of us (L. F. B.) by the Government Grant Committee of the Royal Society.

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THE INVESTIGATION OF THE MAGNETIC PROPERTIES OF NON-HOMOGENEOUS SYSTEMS: PART III, THE PROPERTIES OF FERROMAGNETIC COBALT AND NICKEL IN MERCURY

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ABSTRACT. The ferromagnetic properties of small quantities of cobalt and of nickel dissolved in mercury have been measured by the Gouy method, using a container which was evacuated by a simple method previously described. Cobalt behaved as if it had a specific magnetization of 190 instead of 163·9 and nickel with 45·5 instead of 57·6 c.g.s. units per gm. The experimental results are discussed in the light of a theory, due to Jaanus, of the magnetic behaviour of small quantities of dissolved ferromagnetics.

§ 1. INTRODUCTION

In the preceding communication it has been proved that nickel amalgams which are diamagnetic under ordinary conditions become ferromagnetic on heating to 225° c. The behaviour of cobalt and iron amalgams is in marked contrast, since the latter are always ferromagnetic. The magnetic properties of iron amalgams were investigated recently by Bates and Illsley, who found that in fields of 4 000 to 7 000 oersteds the iron showed a specific magnetization of 130 c.g.s. units per gm. for low concentrations in frozen amalgams at $-78^\circ{\cdot}5$ c., whereas in the case of the bulk metal the magnetization is approximately 220 c.g.s. units per gm. The concentration of iron in these experiments ranged from 0·00093 to 0·0236 gm. in 100 gm. mercury, and it was concluded that a small quantity of iron dissolved in the mercury and rendered the whole body of the amalgam paramagnetic. The magnitude of this paramagnetism, and new theoretical considerations, as well as certain other features of these experiments, indicated that measurements with other ferromagnetic amalgams would be of value. Hence, the investigations described below were made with unheated cobalt amalgams and with nickel amalgams which had been made ferromagnetic by heating them to a temperature above 225° c.

§ 2. EXPERIMENTAL PROCEDURE

The measurements were made by the method adopted by Bates and Illsley, except that each amalgam was placed in a long stoppered tube evacuated by the method described in Part I *, and a more powerful electromagnet was used. The cobalt amalgams ranged in concentration from 0·00093 to 0·0159 gm. cobalt in 100 gm. mercury. Each amalgam was prepared by the electrolysis of a solution of known cobalt-sulphate content, with a pool of mercury as cathode, until the electrolyte was denuded of cobalt. The amalgam was then washed and dried roughly, placed in the containing tube and completely dried by evacuation. The nickel amalgams were prepared as described in the preceding paper (Part II), but after evacuation they were heated to 260° c. and kept at that temperature for one hour.

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* This volume, p. 425.

The amalgam to be investigated was thoroughly mixed to secure uniformity in the distribution of the ferromagnetic constituent, and was frozen rapidly by placing the stoppered tube in powdered " cardice ". The magnetic susceptibility of the amalgam was then found by the Gouy method, using a set of chosen values of the applied field between the plane pole tips of the electromagnet. The tube was suspended by the stopper and was surrounded by a copper tube embedded in solid carbon dioxide within a Dewar flask. In order to obtain trustworthy results the amalgam was melted, mixed anew and frozen again, and the magnetic measurements repeated many times, except in the case of the cobalt amalgam of greatest concentration, where lateral forces made measurements difficult. Indeed, the range of concentration for which the Gouy method may be used is limited by such lateral forces, which, while they are assumed absent in the theory of the method, can nevertheless produce lateral displacements and cause the tube to touch against its surroundings when sufficient ferromagnetism is present. Differences between the individual sets of readings were small, and mean values were taken as the correct values of the susceptibility in the field employed.

§ 3. EXPERIMENTAL RESULTS

In figure 1 the mean values of the measured volume-susceptibilities k of a series of cobalt amalgams are plotted against the reciprocal of the field H between the pole tips. It is clear that with cobalt amalgams an approximately linear relation between k and H is obtained only when H is very large. According to the simple Honda-Owen relation as amended by Vogt(2) we may write

$$k=k_{\infty}+\frac{2c'\sigma_s}{H}-\frac{2Q}{H^2} \qquad \ldots\ldots(1)$$

or

$$\chi=\chi_{\infty}+\frac{2c'}{\rho}\frac{\sigma_s}{H}-\frac{2Q}{\rho H^2} \qquad \ldots\ldots(1\,a),$$

where k_{∞} and χ_{∞} are the volume- and mass-susceptibilities of the amalgam of concentration c' gm. of ferromagnetic metal per c.c. of amalgam when placed in an infinitely strong field, σ_s is the specific saturation intensity of the ferromagnetic in c.g.s. units per gm. and ρ is the density of the amalgam, so that $c'\sigma_s/\rho$ is the saturation magnetic moment of the ferromagnetic in 1 gm. of amalgam. For the low concentrations in these experiments ρ may be taken equal to the density of pure mercury at $-78°{\cdot}5$ c., namely, 14·24 gm. per c.c. The quantity Q will be discussed later.

Bates and Illsley obtained a series of straight lines with iron amalgams of known concentrations when H ranged from 4 000 to 7 000 oersteds, and from them they obtained a value of σ_s for iron. At the same time, they found that χ_∞ increased rapidly, i.e. the amalgams became increasingly paramagnetic, more or less linearly with the concentration of iron. From the experimental values for cobalt which are plotted in figure 1 the values of χ_∞, $c'\sigma_s/\rho$ and $2Q/\rho$ given in table 1 were obtained, using the data obtained with fields of 9 090, 4 965 and 2 060 oersteds for the calculations.

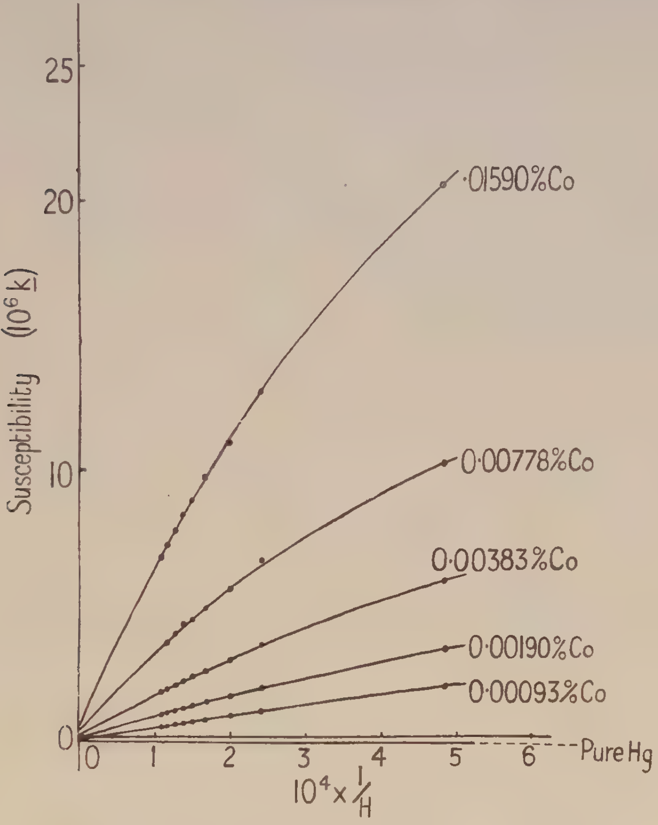

Figure 1. Volume-susceptibility curves for cobalt amalgams.

Table 1. Results for cobalt amalgams

Concentration per cent	$10^6\chi_\infty$	$1000\,\dfrac{c'\sigma_s}{\rho}$	$2Q/\rho$	NI_s
0·00093	−0·147	2·44	1·49	610
0·00190	−0·118	4·45	3·99	897
0·00383	+0·031	7·60	6·75	890
0·00778	+0·234	14·90	19·30	1295
0·01590	+0·435	30·20	39·15	1295

The values of $c'\sigma_s/\rho$ when plotted against the concentration lie close to a linear graph, as shown in figure 2, from which we deduce that σ_s is constant and equal to 190 c.g.s. units per gm. when cobalt is present in mercury in concentrations between 0·004 and 0·016 gm. per 100 gm. amalgam, instead of the value 163·9 units per gm. found at low temperatures for metallic cobalt in bulk. There are indications in figure 2 that at very low concentrations the value of σ_s is even greater.

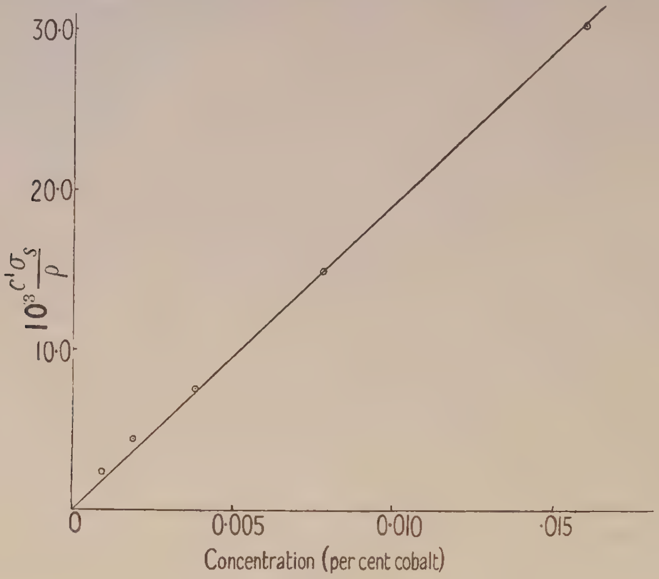

Figure 2. Variation of $\frac{c'\sigma_s}{\rho}$ with concentration in cobalt amalgams.

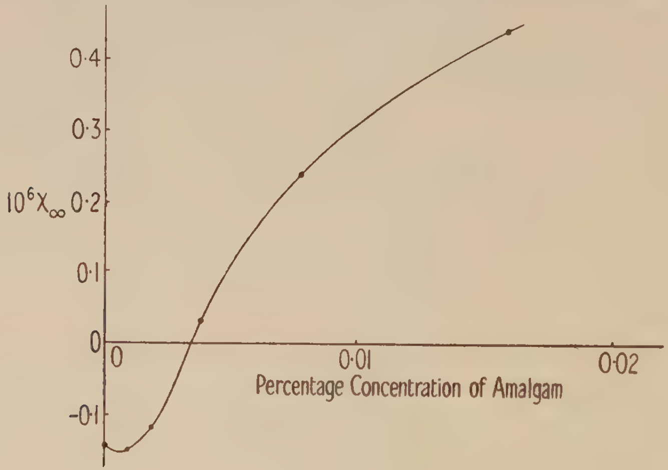

Figure 3. Variation of χ_∞ for cobalt amalgams with concentration.

The values of χ_∞ for cobalt are plotted against the concentration in figure 3, which shows that very weak cobalt amalgams should behave as slightly more diamagnetic than mercury in an infinitely strong field, if the above deductions are correct. However, such deductions would be more reliable if they were made from measurements extending to higher fields, say, of 50 000 to 100 000 oersteds.

The mean values of the measured susceptibilities of a series of heat-treated nickel amalgams of stated concentrations are reproduced as functions of $1/H$ in figure 4. The values of χ_∞, $c'\sigma_s/\rho$ and $2Q/\rho$ given in table 2 were calculated from the experimental values of k obtained with fields of 9 068, 6 660 and 4 135 oersteds.

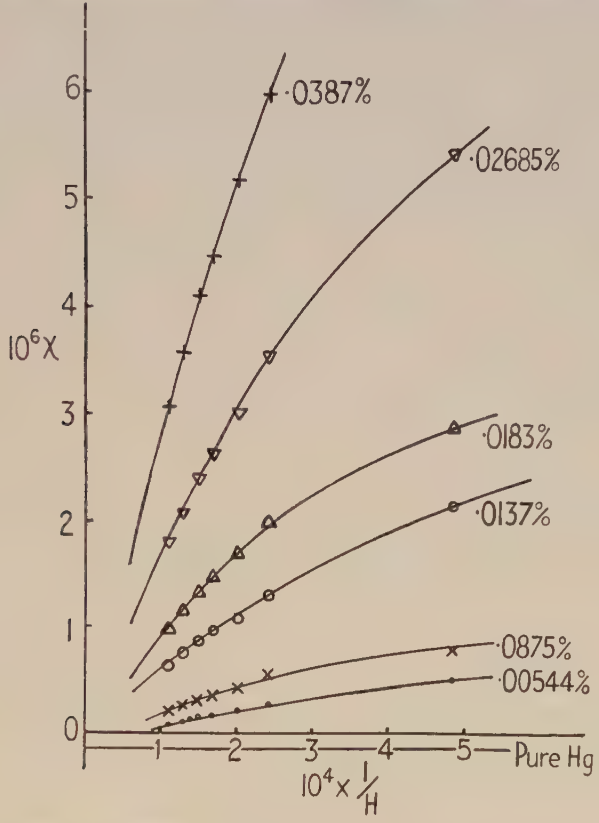

Figure 4. Mass-susceptibility curves for nickel amalgams.

Table 2. Results for nickel amalgams

Concentration per cent	$10^6\chi_\infty$	$1000\,\frac{c'\sigma_s}{\rho}$	$\frac{2Q}{\rho}$	NI_s
0·00544	−0·107	0·888	0·764	861
0·00875	−0·058	1·205	0·489	408
0·01370	−0·1145	3·810	7·35	966
0·01830	−0·099	5·415	9·18	850
0·02685	−0·1235	9·610	16·30	851
0·03870	−0·495	18·425	42·50	1152

From this table the interesting fact emerges that χ_∞ is always negative. This feature would hardly have been expected from a cursory examination of figure 4. No particular significance is attached to the variation of χ_∞ with concentration in view of the method of preparing the nickel amalgams. Also, it is considered that a slight error in the measurements in this case would have had a very big effect on the values of χ_∞ for the weaker concentrations. The large negative value of χ_∞ for the most concentrated amalgam will be discussed later, in the light of the theoretical discussions which follow.

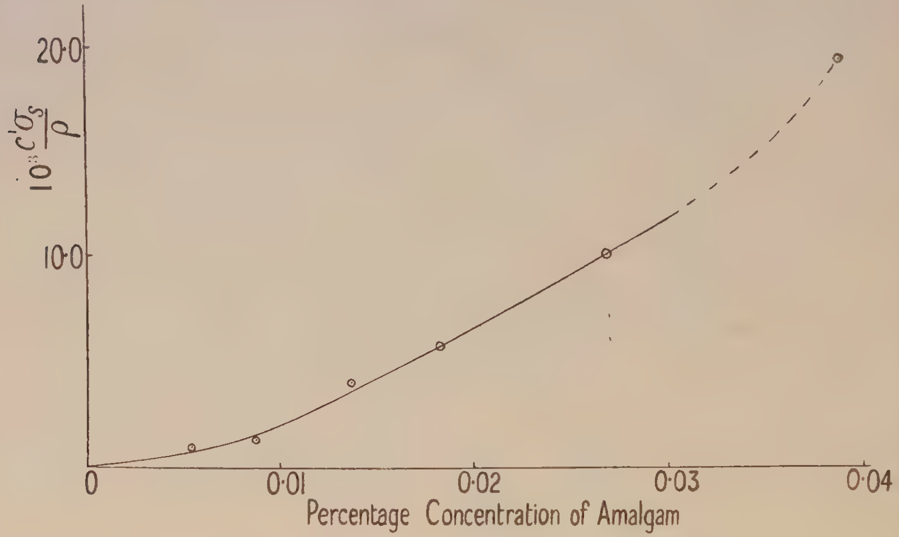

Figure 5. Variation of $\frac{c'\sigma_s}{\rho}$ with concentration of nickel in amalgam.

The variation of $c'\sigma_s/\rho$ with concentration of nickel is shown in figure 5, whence we deduce that in amalgams of concentration between 0·01 and 0·03 gm. nickel per 100 gm. amalgam σ_s is approximately 45·5 c.g.s. units per gm. instead of 57·6 units per gm. as found at low temperatures for metallic nickel in bulk.

§ 4. THE JAANUS THEORY

Vogt's derivation of equation (1) need not be reproduced here, as it is readily available elsewhere, but it is desirable to discuss briefly another method of treating the problem of the magnetic behaviour of small quantities of dissolved ferromagnetics which, in some respects, is rather more general. In Vogt's treatment, which is applicable to measurements by the Gouy method, the ferromagnetic is assumed to be saturated in the main field, notwithstanding the fact that it is extremely difficult to saturate a short thick specimen and that we have no knowledge of the shape of the individual particles of the ferromagnetic, and, consequently, no knowledge of their demagnetization coefficients. Jaanus (3) therefore assumed that each particle had a demagnetization coefficient N and a coercivity h. Hence, when the applied field is H the effective field acting on a particle is $H_e = H - NI$. He also assumed that the Rayleigh law ⁽⁴⁾ was obeyed in the form given by Fröhlich, viz.,

$$I = H_e/(a + bH_e),$$

where a and b are constants (this, of course, is not the form in which the law is usually stated). Then, assuming further that

$$I = 0{\cdot}3 I_s \text{ when } H_e = 1{\cdot}3h$$

and $\quad I = I_s$ when H is very large,

it follows that $\quad I = I_s H_e/(3h + H_e)$

with sufficient accuracy. The experimental value of the susceptibility to which the ferromagnetic would give rise is therefore given by

$$k' = I/H = \frac{1}{2N}\left[1 + \frac{3h + NI_s}{H} - \sqrt{\left(1 + \frac{2(3h - NI_s)}{H} + \frac{(3h + NI_s)^2}{H^2}\right)}\right] \quad \ldots\ldots (2),$$

which clearly depends on both N and h.

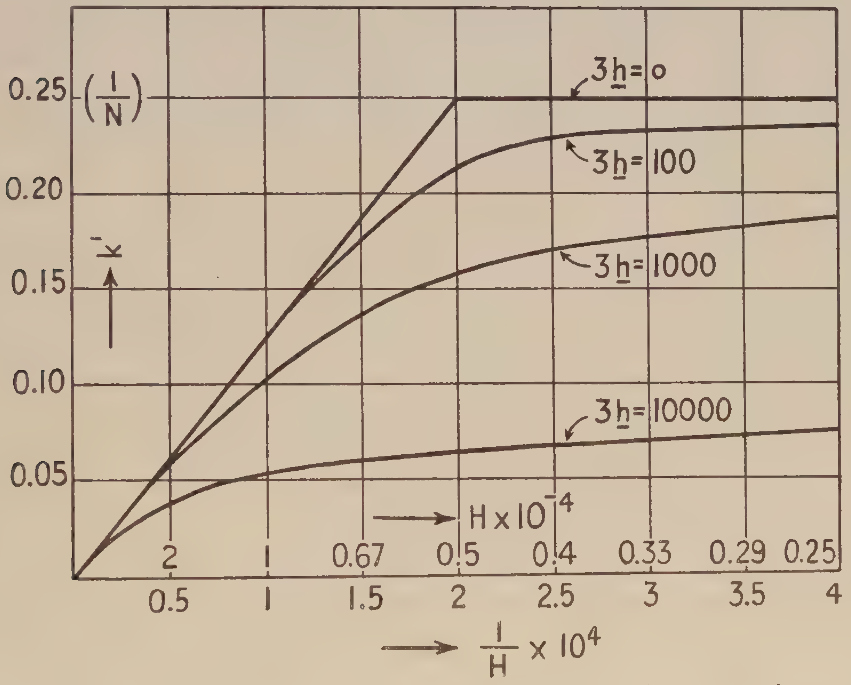

Figure 6. Theoretical variation of volume susceptibility of ferromagnetic impurity with $1/H$.

The way in which k' varies with $1/H$ for certain chosen values of h with $N = 4$, corresponding to particles which are roughly spherical in shape, is shown in figure 6. These curves represent the behaviour which should be found in the case of observations made by the Curie method, i.e. with a small specimen in a non-uniform field. It is seen that with very small values of h the straight line passing through the origin breaks sharply when $H=NI$, i.e. when $k'=1/N$. The Jaanus treatment shows us that it is impossible to get a straight line for low values of H unless N is small, i.e. unless the magnetic particles are elongated. The high values of k' given in the figure arise because they refer to 1 c.c. of ferromagnetic; in ordinary experiments proportionate values corresponding to the low concentration of the ferromagnetic in the specimen are, of course, observed.

For present purposes the Jaanus treatment must be extended to cover measurements made by the Gouy method, wherein the applied field ranges from H perpendicular to the axis at one end of a cylindrical specimen to practically zero at the other end. In this case, if c denotes the volume of ferromagnetic in 1 c.c. of the specimen (amalgam) we find that

$$k=k_{\infty}+\frac{c}{2N}+\frac{c}{N}\frac{(3h+NI_s)}{H}$$
$$-\frac{c}{2NH^2}\left[(H+3h-NI_s)(H^2+2H(3h-NI_s)+(3h+NI_s)^2)^{\frac{1}{2}}\right.$$
$$\left.+12hNI_s\log_e\frac{H+3h-NI_s+(H^2+2H(3h-NI_s)+(3h+NI_s)^2)^{\frac{1}{2}}}{\sqrt{(12hNI_s)}}\right] \quad \ldots\ldots(3).$$

For the special case $(3h+NI_s)<H$ we may expand the first term in the square brackets and neglect the logarithmic term, so that, finally,

$$k=k_{\infty}+\frac{2cI_s}{H}-\frac{cNI_s^2}{H^2}$$

or

$$k=k_{\infty}+\frac{2c'\sigma_s}{H}-\frac{c'\sigma_s}{H}\frac{NI_s}{H} \quad \ldots\ldots(4).$$

Comparing equations (1) and (4) it is seen that they are of the same form, but the extended Jaanus treatment indicates that only when $NI_s/H \ll 2$ should a linear relation between k and $1/H$ be found. The quantity Q in equation (1) is approximately equal to the area between the initial $\{I, H\}$ curve and the I axis, for the conditions specified above. This area is practically equal to $\frac{1}{2}c'\sigma_s \times NI_s$ or to $\frac{1}{2}$(saturation intensity of magnetization of ferromagnetic in 1 c.c. of amalgam) $\times NI_s$, since the area between the $\{I, H\}$ curve and the line drawn at an angle of $\tan^{-1}N$ to the I axis can be assumed to be small. Hence, it is clear that in these circumstances the terms in $1/H^2$ of equations (1) and (4) are really in good accord. Consequently, if $NI_s/H \ll 2$ the third term in equation (4) may be neglected and a linear relation between k and $1/H$ is then obtained.

§ 5. DISCUSSION OF RESULTS

Returning to table 1 it is seen that the values of NI_s extend from 600 to about 1 300, so that the condition $NI_s/H \ll 2$ was not satisfied in the experiments and the non-linear graphs of figure 1 are therefore readily explained. On the other hand, the condition $(3h+NI_s)<H$ appears to have been satisfied, in spite of the fact that cobalt in bulk usually possesses high coercivity. Assuming that the value of I_s for cobalt is 1 420 c.g.s. units per c.c., a value which is lower than that

deduced from these experiments, then N ranges from 0·42 to 0·92. In other words, a sudden kink in the curve for the special case $h=0$ such as is shown in figure 6 would not be possible in these experiments, so that equations (1) and (4) may be regarded as quite satisfactory in the case of cobalt.

In the case of nickel, however, while the condition $(3h+NI_s)<H$ was satisfied with the fields above 4 000 oersteds, it was not satisfied with a field of 2105 oersteds with which the furthermost points to the right on all but one of the graphs of figure 4 were obtained. Indeed, when calculations of $c'\sigma_s/\rho$, $2Q/\rho$ and χ_∞ are made with the data for fields of 9 068, 4 135 and 2 105 oersteds, χ_∞ is in many cases much more diamagnetic than mercury and NI_s is in many cases of the order of 2 000. This means that measurements with low fields in the case of nickel amalgams are useless. Taking the value of I_s for nickel to be 500 c.g.s. units per c.c., the data of table 2 show that N ranges from 1·2 to 2·3, so that we have a further reason for the unsatisfactory nature of the measurements made in low fields. It is significent that the amalgam of greatest concentration gives the highest value of N and the most extreme value of χ_∞, presumably because we have very much larger groups of nickel atoms involved. On the whole, then, it is fair to conclude that the Jaanus treatment gives a fairly complete insight into the behaviour of ferromagnetics in weak concentration in solid mercury.

One further point remains to be mentioned. Bitter and Kaufmann (5) have recently examined the ferromagnetic behaviour of iron dissolved in copper to the extent of 0·003 to 0·71 per cent, using a solenoid of special design to produce fields of 10 000 to 20 000 oersteds. They used the Gouy method and found definite hysteresis effects with an associated remanence small compared with the saturation magnetization. Moreover, the initial susceptibility was found to be approximately constant and equal to $I_s \times 10^{-3}$ for fields up to a few hundred oersteds, and saturation was not complete until the highest fields were reached. In our experiments we did not observe any hysteresis effects except in the case of the nickel amalgams, where we observed a very slight change in the initial zero, i.e. in the apparent mass of the specimen, after the highest field was applied for the first time and the magnet current switched off, leaving a very low residual field. In our view, hysteresis effects could have played only a very minor part in our work.

§ 6. ACKNOWLEDGEMENT

The magnet and much of the apparatus used in the above investigation were purchased by grants to one of us (L. F. B.) from the Government Grant Committee of the Royal Society.

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VIBRATIONS OF FREE SQUARE PLATES: PART II, COMPOUNDED NORMAL MODES

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ABSTRACT. The nodal designs obtainable on free square plates which cannot be included among the seven normal classes of figures (see *Proc. Phys. Soc.* **51**, 831 (1939)) usually consist of two compounded modes of vibration of near period for which the sum m^2+n^2 is approximately equal. Such combination of modes is possible because the internal damping of the material of the plate reduces the sharpness of resonance and because the material and dimensions of the plate are seldom ideally uniform. The observations are in close agreement with the theory proper to a thin elastic plate, a conclusion which may be contrasted with the case of the circular plate (see *Proc. Phys. Soc.* **50**, 70 (1938)) where, for reasons given, the observations made on higher tones are not in agreement with this theory.

§1. INTRODUCTION

Complicated nodal designs sometimes occur on vibrating free square plates which cannot be recognized as belonging to any of the normal classes. It is shown below that such designs generally consist of two compounded modes of vibration, the periods of which are nearly equal.

Before establishing this conclusion it was necessary to be familiar with the normal nodal figures, and to have available a table of the corresponding natural frequencies. A full account of the systematic observations which have been made on these subjects has been published recently (1), in which the main facts regarding the classes of nodal symmetry were collected in a short summary which for convenience of reference is reproduced below, in table 1. The notation employed in the previous paper, $m\,|\,n+$ and $m\,|\,n-$, whereby any particular vibrating mode may be specified, is used again, the letters o and e indicating whether the numbers m and n are odd or even. The connexion between this notation and the equation giving the approximate nodal systems,

$$\omega=Au_m(x)u_n(y)\pm Bu_n(x)u_m(y)=0 \text{ (2), (3), (4)} \qquad \ldots\ldots(1),$$

is obvious.

In this expression ω is the displacement of the plate at the point (x, y) and the functions u are those proper to a free bar of length equal to the side of the plate (2). Except when one of the values m, n is odd and the other is even, the amplitude constants A and B must be equal to one another.

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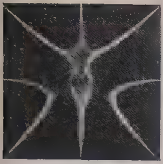
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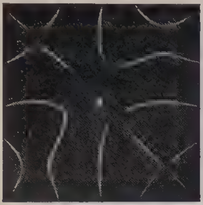
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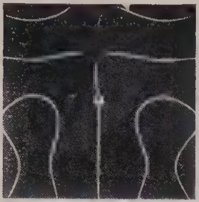
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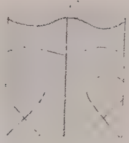
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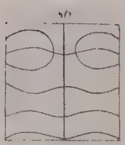
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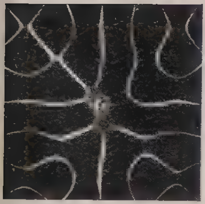
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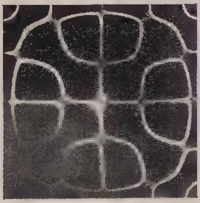
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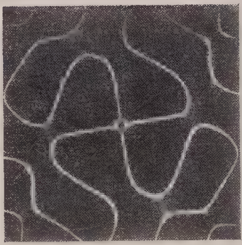
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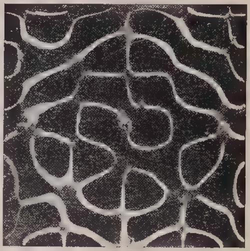
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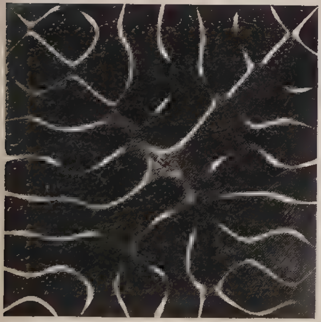
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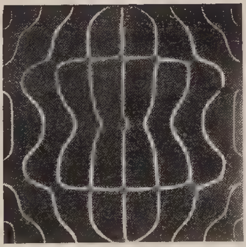
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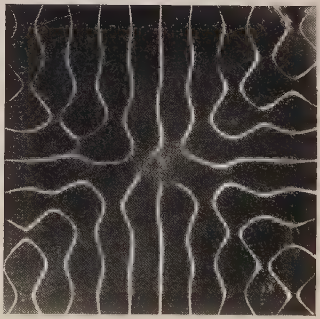
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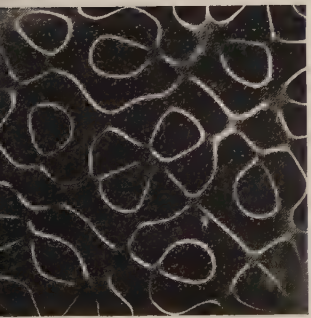
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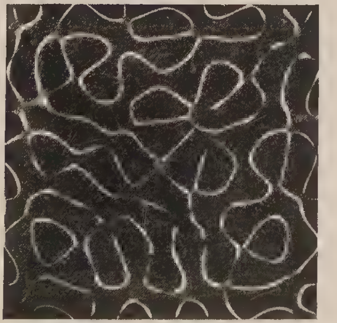
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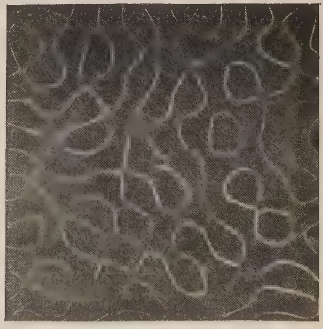
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Plate 1.

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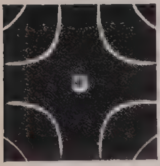
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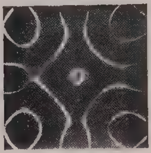
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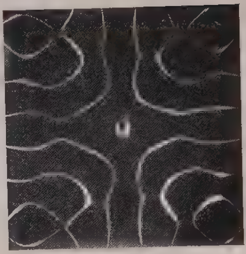
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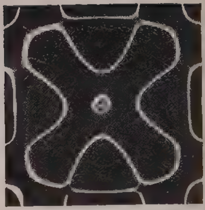
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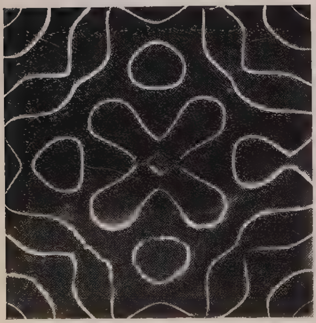
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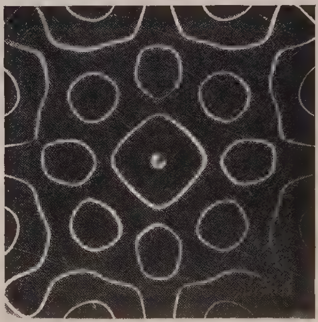
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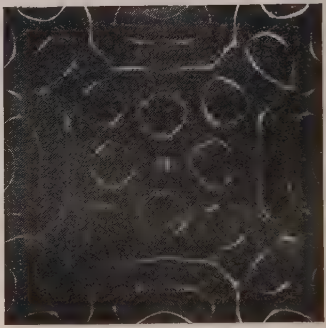
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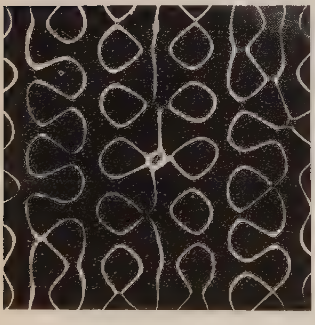
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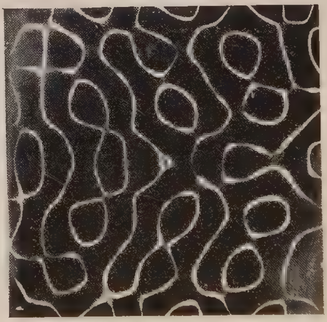
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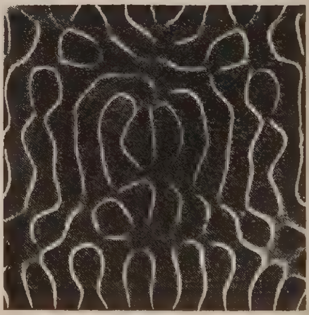
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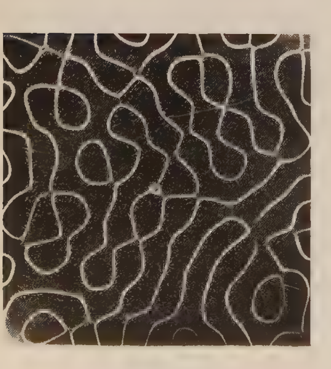
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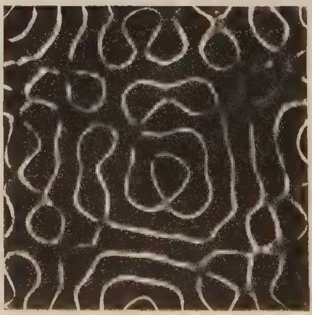
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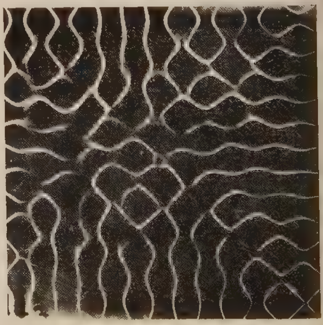
28

Plate 2.

The rules whereby any nodal figure, after being placed in its appropriate class, may be further identified are also given in the former paper. It may be recalled that, except when both diameters are nodal, the value of $m+n$ may be obtained by counting the number of nodal lines across a diameter, while the value of m (or n) is usually found by counting along an edge of the plate.

According to observation and theory (except in the case of the few gravest tones where changes in Poisson's ratio have an appreciable effect on the relative frequencies) those vibrating modes for which the sum m^2+n^2 is identical have approximately, but not exactly, the same vibration frequencies. We may therefore suppose that nodal figures which do not correspond to any of the seven normal classes of table 1 are compounded from two or more such normal modes. This compounding of modes of near period often occurs in the case of the free circular plate (5), and the reason it is possible is because the sharpness of resonance is reduced by the internal damping of the material of the plate. Any want of uniformity in either the material or the dimensions of the plate may also be favourable to the production of compounded modes.

Table 1. The seven classes of nodal symmetry of free square plates

e denotes that the values of m and n are even, and *o* that they are odd

Specification of vibrating mode	Condition at centre	Further details of nodal lines at or near centre	Rotational symmetry	Class abbreviation symbol
$m=n$				
1 $o\|o$	Node	Parallel to edges	90°	+
2 $e\|e$	Antinode	Parallel to edges	90°	□
$m\neq n$				
3 $o\|o-$	Node	Diagonals and medians	90°	✳
4 $e\|e-$	Node	Diagonals	90°	×
5 $o\|o+$	Node	Medians	90°	+
6 $e\|e+$	Antinode	Closed figure	90°	○
7 $e\|o+$ or $-$	Node	One diagonal	180°	╱ or ╲

The only cases, as far as I am aware, of classified compounded nodal figures on free square plates are the two drawings of Chladni (6), which are reproduced in figures 4 and 5 of plate 1. Their recognition is due to Wheatstone (7).

§ 2. EXPERIMENTAL RESULTS

The number of nodal designs which may be obtained on square plates is limitless. Those which cannot be placed among the normal figures belong to compounded modes of vibration. In practice, also, it is not unusual to find figures which have been distorted by the central support and, in passing to higher overtones, complicated figures which are caused by irregularities in the texture and dimensions of the plate. A representative collection of such designs is given in figures 1 to 28. They may be examined in connexion with the data of table 2, where the classification $m_1|n_1, m_2|n_2$ is given in the second column and the corresponding frequencies (obtained by experiment⁽¹⁾ and expressed in relation to the fundamental 1|1 tone taken as unity) are given in the third column. From the last two columns of the table it will be seen that $m_1^2+n_1^2$ is approximately, and in some cases exactly, equal to the corresponding value of $m_2^2+n_2^2$.

Table 2

Some compounded normal modes of vibration of free square plates

<table>
<tr><th>Figures</th><th>Component modes $m_1|n_1, m_2|n_2$</th><th>Experimental frequencies relative to 1|1 tone=1</th><th>$m_1^2+n_1^2$</th><th>$m_2^2+n_2^2$</th></tr>
<tr><td colspan="5">Plate 1</td></tr>
<tr><td>1</td><td>3|0, 3|1</td><td>5·1, 5·3</td><td>9</td><td>10</td></tr>
<tr><td>2</td><td>5|0, 5|1</td><td>15·8, 15·8</td><td>25</td><td>26</td></tr>
<tr><td>3</td><td>5|1, 2 5</td><td>16·6, 19</td><td>26</td><td>29</td></tr>
<tr><td>4</td><td>5|1, 2|5</td><td>16·6, 19</td><td>26</td><td>29</td></tr>
<tr><td>5</td><td>3|5, 6|1</td><td>23·3, 23·9</td><td>34</td><td>37</td></tr>
<tr><td>6</td><td>7|0, 7|1</td><td>32·5, 32·4</td><td>49</td><td>50</td></tr>
<tr><td>7</td><td>5|5, 7|1</td><td>35, 32·4</td><td>50</td><td>50</td></tr>
<tr><td>8</td><td>5|5, 7|1</td><td>35, 32·4</td><td>50</td><td>50</td></tr>
<tr><td>9</td><td>8|3, 7|5</td><td>50·5, 53</td><td>73</td><td>74</td></tr>
<tr><td>10</td><td>9|0, 9|1</td><td>55·2, 55·8</td><td>81</td><td>82</td></tr>
<tr><td>11</td><td>9|2, 7|6</td><td>59, 61·7</td><td>85</td><td>85</td></tr>
<tr><td>12</td><td>11|1, 11|0</td><td>86·1, 84</td><td>122</td><td>121</td></tr>
<tr><td>13</td><td>10|5, 11|2</td><td>90, 89</td><td>125</td><td>125</td></tr>
<tr><td>14</td><td>12|4, 11|6</td><td>116, 115</td><td>160</td><td>157</td></tr>
<tr><td>15</td><td>13|2, 12|5</td><td>124, 122</td><td>173</td><td>169</td></tr>
<tr><td colspan="5">Plate 2. Figures showing distortion due to central screw</td></tr>
<tr><td>16</td><td>4|2</td><td>13·1</td><td>20</td><td></td></tr>
<tr><td>17</td><td>6|2</td><td>27·1</td><td>40</td><td></td></tr>
<tr><td>18</td><td>8|2</td><td>46·6</td><td>68</td><td></td></tr>
<tr><td>19</td><td>4|4, 6|0</td><td>21·5, 23</td><td>32</td><td>36</td></tr>
<tr><td>20</td><td>10|2, 8|6</td><td>73, 73</td><td>104</td><td>100</td></tr>
<tr><td>21</td><td>10|4</td><td>82·9</td><td>116</td><td></td></tr>
<tr><td>22</td><td>12|2, 10|6</td><td>105, 99</td><td>148</td><td>136</td></tr>
<tr><td>23</td><td>13|0, 12|3</td><td>119, 110</td><td>169</td><td>153</td></tr>
<tr><td colspan="5">Irregular figures</td></tr>
<tr><td>24</td><td>11|6 etc.</td><td>115</td><td>157</td><td></td></tr>
<tr><td>25</td><td>13|2, 11|7</td><td>124, 124</td><td>173</td><td>170</td></tr>
<tr><td>26</td><td>11|7, 13|2</td><td>124, 124</td><td>170</td><td>173</td></tr>
<tr><td>27</td><td>13|4, 11|8</td><td>132, 136</td><td>185</td><td>185</td></tr>
<tr><td>28</td><td>14|0, 14|1</td><td>141, 143</td><td>196</td><td>197</td></tr>
</table>

Figures 1 to 15 consist of two compounded normal modes which have been recognized by inspection of the nodal lines assisted by a knowledge of the vibration frequencies. The $m|o$, $m|1$ design is a common one, as may be seen from figures 1, 2, 6, 10 and 12; the symmetry when both component modes belong to the same class may be noted. Thus the $o|o$, $o|o$, figure 8, retains the two nodal lines through the centre and the rotational symmetry of 90° which is typical of the $o|o$ class, see table 1, and the $o|e$, $o|e$ figures 11 and 13 retain the one nodal diameter and rotational symmetry of 180°. In other combinations the rotational symmetry is generally lost—for example see figures 1, 3, 4 and 5; the mirror symmetry of these figures, however, is interesting.

Figures 16 to 22 were, after some consideration, classified as $e|e+$ designs which have been distorted by the central support. If this surmise is correct, they are not actually due to free vibrations of the plate, but their regularity—the rotational symmetry is one of 90°—and the fact that they are familiar designs are justification for including them in this paper.

Figures 24 to 28 are typical of the irregular designs which are sometimes found for higher overtones; the corresponding frequencies are as much as 115 to 143 times that of the fundamental tone. The classification of the more complicated figures is a little uncertain.

§ 3. CONCLUDING REMARKS

Comparison with circular plate. It is noteworthy that whereas the observed natural frequencies on square plates are in agreement with theory, it is otherwise for a circular plate (8) where in passing to higher overtones the discrepancy between observation and theory becomes increasingly marked. It is not difficult to see why this is so, for whereas the maximum number of nodal lines which may pass through the centre of a square plate is four, an indefinitely large number of nodal diameters is possible for a circular plate. Now the Kirchhoff theory (2) of the circular plate and the Rayleigh-Ritz theory (2), (4) of the square plate apply only to plates in which the thickness is small in comparison with the distance between adjacent nodal lines. It is evident then that the circular plate ceases to vibrate according to the laws of thin plates when the number of nodal lines through the centre becomes considerable. A square plate, on the other hand, of the dimensions generally employed for producing Chladni designs, will obey these laws except for much higher overtones than those which have been considered above.

Poisson's ratio. We have, in this paper, been concerned with the higher rather than with the lower overtones of vibrating brass plates. The systematic experimental study of free square plates is not yet complete. It remains to obtain more precise measurements of the graver tones on plates made of different materials and to explore the possibilities of finding Poisson's ratio by an acoustical method.

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THE VELOCITY OF PROPAGATION OF WIRELESS WAVES OVER THE GROUND

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ABSTRACT. A technique is described for the measurement of the rate of travel of high-frequency impulses over the ground. Two transmitters 60 km. apart and operated off a common A.C. supply provided the signals, and the time intervals between the arrival of the local and distant impulses were measured at each station. From these the mean rate of travel could be determined. The measurements were made on a cathode-ray tube in a manner similar to that used in ionospheric work, and the precautions necessary to secure accurate results are described.

Results are given which show that the velocity of propagation is within a few per cent of that of light; and it is concluded that the experiments of other workers which yielded a much smaller value for the velocity are subject to some error.

§ 1. INTRODUCTION

Until recently it has been generally assumed that wireless waves travel over the ground with the velocity of light. For example, in ionospheric experiments in which the time delay between the arrival of a high-frequency impulse over the ground and after reflection from the ionosphere is measured, it is usual to assume that the velocity over the ground path is the same as in free space in computing the equivalent height of reflection.

It has, however, been realized that the electrical properties of the ground may influence the velocity of propagation. If we take the ideal case of a plane wave travelling over a flat earth, as considered by Zenneck(1), it is possible to form an approximate expression for the group-velocity for any earth constants, and to show that for average ground this velocity is not likely to depart from that of light by more than 2 or 3 per cent. This is small enough to be insignificant in ordinary ionosphere measurements, and it is presumably for this reason that little attention has been paid to it either experimentally or theoretically.

Certain experiments have, however, been made. In 1936 Colwell, Hall and Hill(2) made tests on the velocity of propagation of high-frequency impulses over the ground, in which they measured the time of travel of the waves to a distant receiver and back again. They concluded that the velocity of propagation was variable and was about 2/3 that of light, a result considerably less than the anticipated value. More recently Ross and Slow⁽³⁾ have measured the velocity of phase propagation over the ground by observing the phase difference between the E.M.F.s in two aerials spaced in the direction of transmission of the wave. The E.M.F.s were applied to the two pairs of plates of a cathode-ray tube, and from the shape of the ellipse produced and the frequency of the wave the velocity could be calculated. Their results indicated a velocity equal to that of light to an accuracy of about 5 per cent. A similar result has recently been derived by Brown⁽⁴⁾ in America by studying the field distribution in the neighbourhood of a directional aerial.

A somewhat different method of determination has been used by Mandelstam and Papalexi⁽⁵⁾ in Russia. A wave of variable frequency was transmitted from one station and received at another many kilometres away, where its frequency was changed in a fixed ratio not very different from unity. This new wave was retransmitted to the first station, and by applying it to one pair of plates of a cathode-ray tube while the outgoing wave was applied to the other pair, a Lissajous figure was produced. As the frequency of the first wave was varied this figure changed, and the number of cycles of phase covered for a given change in frequency of the outgoing wave could be determined. The experiment is analogous to the early "fringe" experiments of Appleton and others, and the authors show that, as in their work, the measurements of phase change should yield the group-velocity of the waves. The method involves a number of experimental difficulties, but the writers have obtained very consistent results, and the technique appears capable of giving a high degree of accuracy. It has been applied to transmission over various types of ground and over sea, and the values obtained for the velocity, though differing slightly, are all found to be within 1 or 2 per cent of the velocity of light.

The very much lower velocity of propagation found by Colwell and his associates is surprising in view of these measurements. If a short wave-train as used by these experimenters does in fact travel with a velocity of only about 60 per cent of that of light, there is need for interpretation of the frequency-change results of Mandelstam and Papalexi, as well as revision of other experimental work involving ground-wave velocities. It was with the object of providing further experimental data on this question that the work described below was carried out.

§ 2. VELOCITY MEASUREMENT USING PULSES

The principle of the velocity determination used was similar to that employed by Colwell, Hall and Hill. It consisted in transmitting high-frequency impulses from two well-separated stations, and receiving at each end the signal from the local transmitter and also that from the distant one. The time intervals between the arrival of the two impulses at either station were then measured, and from these the mean velocity over the path between the two points could be determined. In our experiments the receivers were located one or two kilometres from the transmitters, and these distances were allowed for in the calculation in the way indicated in § 4. Synchronisation of the transmitted impulses was conveniently effected by locking each sender to the A.C. supply mains, these being common to the two localities: apart from certain fluctuations of phase which will be discussed later, this provided a satisfactory datum for the measurements, and obviated the need either for an alternative link between the two stations or for a manually controlled synchronising system.

The technique of measuring time delays by means of high-frequency impulses has been widely developed in ionospheric work. It is easy to see, however, that a much higher degree of accuracy is required in our present measurements than in those on the ionosphere. This is for two reasons. In the first place, random fluctuations in the heights of reflection in the ionosphere are always present, so that great precision cannot usefully be employed; and in the second place, we are restricted in this work to a distance between the two stations short enough to allow a ground wave of sufficient strength to be received. To avoid interfering with broadcasting, transmissions were confined to wave-lengths less than 200 metres,* which meant that adequate strength could not be obtained beyond about 60 km. Suitable apparatus was available at Cambridge and Chelmsford, which are separated by about this distance, and these stations were therefore chosen. But it is clear that if the time of travel is to be measured to, say, 1 per cent over this distance, the precision of timing at each end must be such as to resolve path differences of the order of $\frac{1}{2}$ km. It should be mentioned that in recent measurements on tidal variations in the E region, Appleton and Weekes have achieved an accuracy of this order, but they do not claim any such precision in the absolute magnitudes of the time delays involved. Careful consideration had therefore to be given to the possible sources of error in the measurement of time intervals between impulses. With the type of apparatus normally employed, and which was available for these experiments, these are of three kinds:

1. Errors in the time scale on the oscillograph.
2. Delay of the wave-train in passing through the receiver, which may vary with amplitude and frequency of the signal.
3. Uncertainty as to the exact point on the pulse envelope at which the measurement is made.

The time scale at each station was provided from a local oscillator. At one station this had a frequency of 1500, and at the other 3000 cycles per second, either being a convenient value for relating measurements on the tube to equivalent paths of the waves. Each oscillator was synchronised to the time-base sweep, which had a recurrence frequency of 50 cycles per second. The mains A.C. supply, linked to the national "grid", provided the standard of frequency. By comparing this with a tuning fork having stability of about 1 part in a million it was found that variations from its mean 50-cycle frequency were never sufficient to introduce appreciable errors. But care was essential to ensure that the locking did not pull the oscillator slightly from its natural frequency, which would cause it actually to run at an incorrect speed between synchronising impulses. This was safeguarded at both ends by adjusting the frequency of the oscillator (with no locking voltage applied) until it gave an exactly stationary pattern on the oscillograph, and then applying as little synchronising voltage as was necessary to maintain a steady state. In this way any tendency of the oscillator to drift from its true frequency was at once detected.

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* The experiments of Colwell, Hall and Hill (loc. cit.) were made on wave-lengths of 125 and 186 metres.

The possibility of errors arising from delay of a wave-train in the receiver was examined carefully. At each station it was inevitable that a strong ground-ray should be received from the nearby transmitter and a weak signal from the distant one, with the result that the former saturated the receiving amplifier at an earlier stage than the latter. This, combined with the finite time required for a wave-group to travel through a series of circuits, implied that the time measurement between the pulses at the output of the receiver might be in error.

n order to guard against such errors it was arranged that each signal should be brought to the same amplitude at the input terminal of the receiver (as indicated by a given deflection on the tube) before measurement of its position on the time-base was made. At one station this was conveniently done by receiving on a loop aerial connected through a goniometer to the receiver; either the orientation of the loop or the setting of the goniometer could then be used to control the signal level. At the other station the length of aerial connected to the receiver was varied to provide the necessary control. In both cases well-screened receivers were used so that even the strong local signal should not enter except by the aerial circuits. The alternative procedure of varying the gain control of the receiver was not considered trustworthy owing to the reaction on the H.T. supplies when the anode currents of the valves were changed, and, more particularly, to the onset of non-linearity at an early stage in the receiver when picking up the local ground-ray.

In the early experiments the two transmitters were set to exactly the same frequency. This ensured that any dependence of the time lag in the receiver on frequency should not influence the results. In later tests, however, it was found preferable to use two slightly different frequencies so as to avoid interference by echoes from the ionosphere with the distant ground-ray signal, and the possibility of inaccuracy through imperfect tuning to either signal therefore arose. It was found that, provided the intermediate frequency was correctly adjusted to the centre of the band-pass, there was no detectable error introduced through the receiver; and the measurements were therefore made taking this precaution.

The third source of inaccuracy, namely, uncertainty as to the exact point of the envelope of the pulse at which measurements should be made, was also taken into account. At first the observations at one station were made by differentiating the pulse E.M.F. before applying it to the oscillograph, since this gives a well-defined point on the time-base for measurement; but it was realized that unless this were done using identical circuits at both ends, any differences in the shape of the pulse envelope from the two transmitters would cause serious errors in the results. The difficulty was overcome by making all measurements on the steep rise of the pulse, uniformity being ensured by taking a point 1/10 of the way up the side in each case. With this precaution at both ends the results should be independent of the shape of either pulse.

§ 3. EXPERIMENTAL PROCEDURE

As mentioned above, the experiments were carried out between Cambridge and Chelmsford. At Chelmsford the receiving station was situated 4·2 km. from the transmitter; at Cambridge two receivers were available, one 0·15 and the other 1·2 km. from the transmitter, and the different distances of these were used to investigate the effect of proximity of transmitter and receiver.

Each receiving station was equipped for complete control of the local transmitter, both as regards frequency and phase of the pulse, and, in addition, simple signalling could be carried out. Vertical aerials with suitable capacity tops were used to obtain the greatest possible ground-ray intensity at the distant receiver.

The procedure in any experiment was as follows :—The Cambridge transmitter was set to a frequency of about 1·8 Mc./sec., the exact value being chosen to avoid interference from other stations, and the Chelmsford transmitter was then set either to the same frequency or to a slightly different value, again avoiding interference. The phase of one pulse was then varied until it appeared within one or two milliseconds of the pulse from the other station, and the time-bases were then speeded up at each station to permit accurate measurement of the separation between the pulses. The early experiments were made in the day-time. This was done to ensure the minimum noise level from outside so that the ground-rays should be clearly defined. It was found, however, that small changes in phase between the two transmitters were continually occurring, and this impaired the accuracy of measurement; and since it was suspected that these phase changes might be due to the varying load on the power system, subsequent measurements were made at night. These gave more satisfactory results; but the difficulty arose that at one station the distant ground-ray was obscured by the echoes from the ionosphere due to the local transmitter; even if the pulse phase was adjusted to avoid the main echoes from the E or F region it was found that weak echoes extending right round the time-base caused sufficient interference to hinder the measurement. For this reason slightly different frequencies were used on the two transmitters, and the receivers were tuned before each measurement, as described above. Certain phase variations were present even at night, though of a slower nature than in the day. To reduce the effect of these a time schedule was used, so that measurements should be made simultaneously at the two ends. This was later improved upon by keying the Chelmsford transmitter with a modulation of 1500 cycles/sec. at intervals of two minutes; this served as a timing signal at which observations at each station were to be made.

Since some degree of inaccuracy was necessarily present in the measurements they were repeated a large number of times, extending over several different nights. It was hoped in this way to eliminate the uncertainties introduced by random fluctuations.

§ 4. THEORY OF VELOCITY DETERMINATION

We will describe the transmitters as 1 and 2.

Let the distance from transmitter 1 to the nearby receiver be d_{11} and to the far receiver d_{12}; similarly, let the distance from transmitter 2 to the nearby receiver be d_{22} and to the far receiver d_{21}.

Suppose transmitter 1 sends out a pulse at time t_1 and transmitter 2 at time t_2. Suppose, too, that there is a lag in passing through receiver 1 of τ_1 and in passing through receiver 2 of τ_2.

Denoting by V the velocity, the two pulses observed will be on receiver 1 at times

$$(t_1+d_{11}/V+\tau_1) \quad \text{and} \quad (t_2+d_{21}/V+\tau_1),$$

and on receiver 2 at times

$$(t_1+d_{12}/V+\tau_2) \quad \text{and} \quad (t_2+d_{22}/V+\tau_2).$$

At each end, the time interval between the two pulses is measured. Subtracting, therefore, the result at receiver 1 from that at receiver 2, we obtain the quantity,

$$\Delta=(d_{12}+d_{21}-d_{22}-d_{11})/V,$$

which depends only on V and the various known ground-distances. In our experiments, taking the receiver more remote from the transmitter at Cambridge,

$$d_{11}=1{\cdot}2 \text{ km.} \qquad d_{12}=62{\cdot}8 \text{ km.}$$
$$d_{22}=4{\cdot}2 \text{ km.} \qquad d_{21}=60{\cdot}0 \text{ km.}$$

Thus $$\Delta=2\times 58{\cdot}7/V.$$

The effective ground-distance between the two stations is thus 58·7 km., and this may be compared with the measured time-interval to determine the velocity.

§ 5. DISCUSSION OF RESULTS

In the table are shown the results of one of the night tests, on 18 August 1939. Readings were taken every two minutes, the synchronising being secured by imposing the 1500-cycle note on the Chelmsford transmitter. The readings given for Cambridge are those obtained at the receiver more remote from the transmitter.

The measured pulse separations at each station are expressed in kilometres of equivalent path divided by 2. If the waves travelled with the velocity of light, therefore, the difference between the readings at the two ends would be equal to the effective distance between the stations, 58·7 km. Departures from this value are a direct measure of the extent to which the wave velocity differs from that of light.

The average of all the results in the table is 61·8 km. This implies a velocity of travel of $\frac{58 \cdot 7}{61 \cdot 8}$ c, i.e. 0·95 c. The variations between readings are, however, appreciable, and introduce a probable error in this value of 0·01 c.

This points to a rate of travel of high-frequency impulses about 5 per cent less than the velocity of light, a result somewhat less than the values obtained by Mandelstam and Papalexi for the group velocity. We are not fully convinced, however, that the deviation from c is significant in our results. The values obtained on other nights showed slight differences which did not appear to be the result of real changes in the velocity, and we are led to suspect that some slight systematic error has not been eliminated from the experiments, so that the statistical analysis is inapplicable. We are satisfied that errors of this type are small and that the actual velocity of a high-frequency impulse does not differ by more than 6 or 7 per cent from the velocity of light.

G.M.T.	Pulse separation in km.		Difference (km.)
	Chelmsford	Cambridge	
0124	151·5	87	64·5
0126	152·5	88·5	64
0128	151·5	95	56·5
0130	152·5	96·5	56
0132	156·8	98·5	58·3
0134	157	96	61
0136	160	96	64
0138	161	99	62
0140	162	97	65
0142	158·5	96	62·5
0144	160	100	60
0146	165	102	63
0148	166·5	103	63·5
0150	161	107	54
0152	162	107	55
0154	163·5	101	62·5
0156	173	106	67
0158	173	104	69
0200	172	106	66

Measurements made on the receiver nearer to the transmitter at Cambridge were less consistent than those referred to, and suggested that there was some disturbing influence due to the proximity. On comparing with the station 1·2 km. away they indicated that the local pulse was appearing too early on the oscillograph by a time equivalent to about 7 km. of path. A close investigation revealed that this was due to a surge from the thyratron modulating the transmitter: the discharge of this valve precedes the high-frequency impulse by a very short interval and is propagated to the receiver either on the power mains or otherwise, thus causing the rise of the pulse to appear earlier than it should. This discharge was found to have no influence at the more distant receiver, and we consider that the results obtained there are more reliable. It is important to notice, though, that great precautions would be necessary if the experiments were made with the transmitter and receiver in the same building, as is common in ionospheric work.

The variability in the results given above is largely attributable to the persistent changes in phase of the supply mains, which were present even at night, and which were too rapid to eliminate by the technique of synchronised measuring. In order to obtain more accurate results it would be necessary to use some modified technique such as locking the transmitter at one station to the received signal from the other, but it was not possible to introduce this into the present tests.

Thus our conclusion from the measurements made is that the velocity of propagation of a high-frequency impulse over the ground is within about 7 per cent of the velocity of light. Though the accuracy of the results is less than was desired, we consider that the much smaller value for the velocity obtained by Colwell, Hall and Hill cannot be correct, and that there is no indication of inconsistency between the frequency-change results of Mandelstam and Papalexi and the rate of travel of a short wave-train as used in our tests.

ACNOWLEDGEMENTS

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THE CHARACTERISTICS OF PROTANOMALOUS VISION

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ABSTRACT. The colour vision of 11 protanomalous observers, selected from about 2,000 persons, has been tested in detail. The measurements include the luminosity curve, the mixture curves, the trichromatic coefficients through the spectrum, the hue discrimination curve and the saturation discrimination curve. The observers have been arranged in order of increasing seriousness of the defect, and the hue discrimination results yield a family of curves ranging between that for the normal trichromat and that for the protanopic type of dichromat. The luminosity data, on the other hand, vary little from observer to observer and the mean curve is almost identical with that of the protanope in the red-yellow-green region of the spectrum. This result is difficult to reconcile with the ordinary conception that different degrees of protanomalous defect arise from the magnitude of the red response varying from one observer to another.

§1. INTRODUCTION

During the past thirteen years a series of researches on colour vision has been in progress at the Imperial College, and one of the main lines of work has been the measurement of the characteristics of both normal and defective colour vision. These characteristics include colour-mixture data, luminosity, hue discrimination and saturation discrimination, the measurements having been applied to ordinary trichromats (1), (2), (3), (4), (5), (6), (7), (8), to dichromats (9), and to anomalous trichomats (10). The investigation of Nelson (10) on anomalous trichomats was in the main confined to the deuteranomalous type of observer, while the present paper, which brings this series of investigations to a close, deals only with the protanomalous observer, an observer who is characterized by a lowered luminosity at the red end of the spectrum and a reduced sensitivity to colour differences in the red-yellow-green region. He still, however, requires the use of three colorimeter primaries in order to make satisfactory colour matches, so that he may be regarded as intermediate between the normal trichromat and the protanopic type of dichromat.

The value of the measurements lies in the fact that they provide fundamental quantitative data about the colour-perception process of each observer, data that must depend in a very direct manner on the actual physiological mechanism in retina and brain. It may therefore be anticipated that the analysis and comparison of the different types of colour defect should ultimately play an important part in discovering the nature of the process through which colour perception is mediated. Further, the results are of practical importance in connexion with the elimination of defective observers from certain occupations in which colour is involved. At some point between the normal observer and the anomalous trichromat, a division has to be made between those whose employment in a certain type of job is safe (or possibly economic) and those for whom such employment would be unsafe or uneconomic. The tests reported here are far too elaborate to be used for the routine examination of large numbers of subjects, but it is in the light of these detailed tests that the simpler tests ought to be designed in order to eliminate only those whose colour discrimination is sufficiently poor to justify elimination.

§ 2. APPARATUS AND TECHNIQUE

The apparatus and experimental technique employed in the present investigation are identical with those used by Nelson (10), and his paper should be consulted for a detailed account. As before, the original model of the Wright colorimeter (11) was used, in which a 2° square field is seen by the observer, one half of the field being illuminated by monochromatic light and the other by a mixture of three primaries. The colour coefficients have been recorded as before in terms of the primaries $0{\cdot}65\,\mu$ (red), $0{\cdot}53\,\mu$ (green) and $0{\cdot}46\,\mu$ (blue); the units were adjusted to the W.D.W. system (1), (2), in which equal quantities of red and green are required to match a yellow of wavelength $0{\cdot}5825\,\mu$ and equal quantities of green and blue are required in a match on a blue-green of wavelength $0{\cdot}4940\,\mu$. The luminosity values were derived from the relative luminosities of the three primaries and from the colour matches made throughout the spectrum, allowance being made for the energy distribution, so that the results refer to an equal-energy spectrum. The results on hue discrimination record the smallest wavelength difference between two monochromatic fields that can just be detected as a difference in colour at various points in the spectrum. The measurements on saturation discrimination give the amount of monochromatic light that has to be added to white to produce a just noticeable difference from white. The white light used was the C.I.E. 1931 S_B source and the size of step has been recorded in the usual manner as $\log{(L_w+L_s)/L_s}$, where L_s is the luminosity of the spectral colour that has to be added to the white of luminosity L_w to be just detected.

§ 3. SELECTION OF OBSERVERS

The percentage of protanomalous persons, even among males, is small, so that a very large number of people had first to be tested in order to find those who were of the type required and who were available to make more detailed and prolonged tests. In all some 2,000 observers were examined using Ishihara's tables, and those who showed any deficiency were further tested with a Nagel anomaloscope to determine into which class they fell. Seventeen protanomalous persons were discovered altogether, and of these 11 were able to spare the time to make the detailed observations with which this paper is concerned.

§ 4. RESULTS

The results are given in tables 1 to 11 and a selection of the data are illustrated in figures 1 to 3. The observers have been arranged in order of increasing seriousness of their defect. To determine this order the hue discrimination curve has been chosen as the most reasonable criterion, but it may sometimes happen that an observer has better discrimination in one part of the spectrum than his neighbour in the list, and worse in another. The classification cannot, therefore, be regarded as quite rigid, yet, as can be seen from figure 1, there is no real doubt as to the order in which the observers should be arranged.

Of the other data recorded, the saturation discrimination curves are illustrated in figure 2 and the first six luminosity and mixture curves in figure 3. For comparison, the normal trichromatic hue and saturation curves are included in figures 1 and 2 respectively, together with the hue discrimination curve for the protanope in figure 1. It will be noticed that no values are given for the trichromatic coefficients nor for the mixture curves for the last five observers. This is primarily due to the fact that it was impossible to determine the spectral coefficients between $0{\cdot}53\,\mu$ and $0{\cdot}65\,\mu$ with an accuracy that had any meaning. It can be seen from the corresponding hue discrimination curves that the number of just noticeable steps between these wavelengths is quite small, of the order of 6, so that the determination of any precise shape of coefficient curve or mixture curve is out of the question. It can be compared to the normal observer using, say, $0{\cdot}587\,\mu$ as his green primary and $0{\cdot}593\,\mu$ as his red primary and attempting to measure the coefficients of the colours between those two wavelengths. The data in the blue-green part of the spectrum could be determined with greater, although still reduced, accuracy, and as no significant difference from the other observers was found, the results have been omitted.

Even the coefficient curves of the first six observers show no characteristics of special interest, such as were recorded by Nelson for the deuteranomalous observer. In one or two cases, small irregularities were suspected in the neighbourhood of $0{\cdot}54\,\mu$, but again they occurred in a range of wavelengths of the order of only one just noticeable step, and consequently were not of any real significance. To have included them would have given them undue emphasis, so that the results as tabulated are those derived from smoothed curves, ignoring the one or two small irregularities that were suggested.

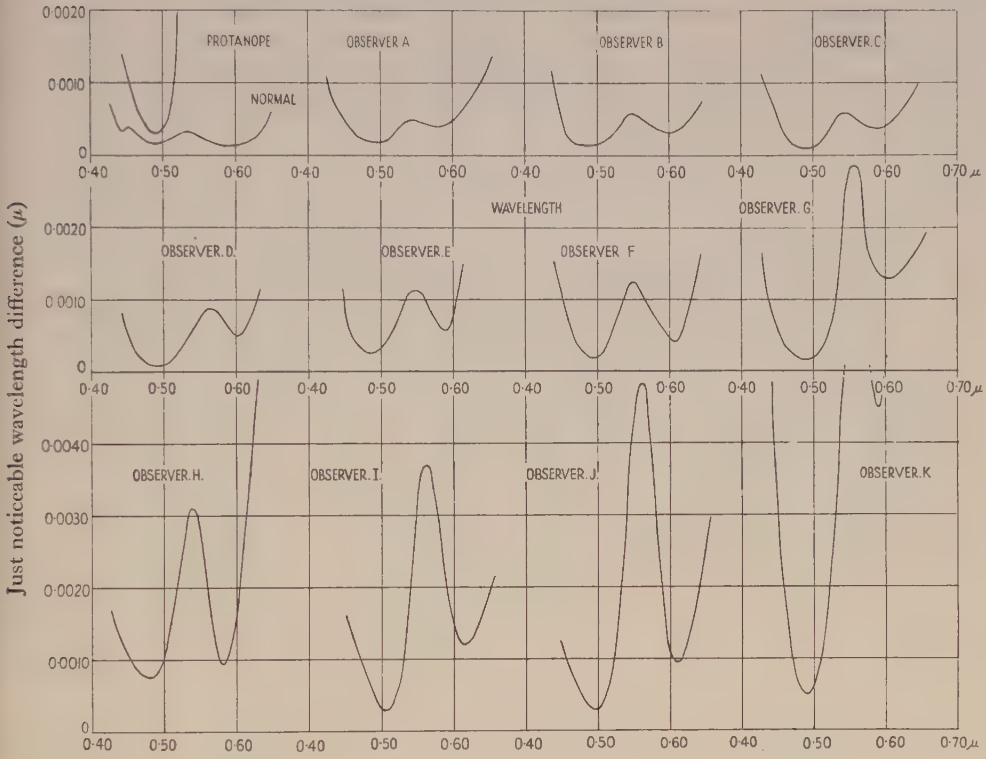

Figure 1. Hue discrimination curves for 11 protanomalous observers arranged in order of increasing magnitude of defect. The first diagram shows the corresponding curves for the normal trichromat and for the protanopic type of dichromat.

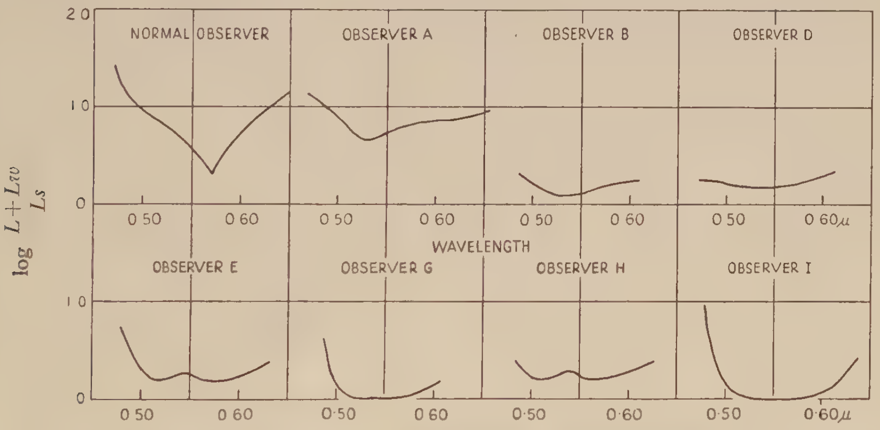

Figure 2. Saturation discrimination curves for seven protanomalous observers. The first diagram shows the curve for the normal trichromat. The ordinate plotted is log $(L_w+L_s)/L_s$, where L_s is the luminosity of the spectral colour that has to be mixed with white of luminosity L_w to be just distinguishable from white.

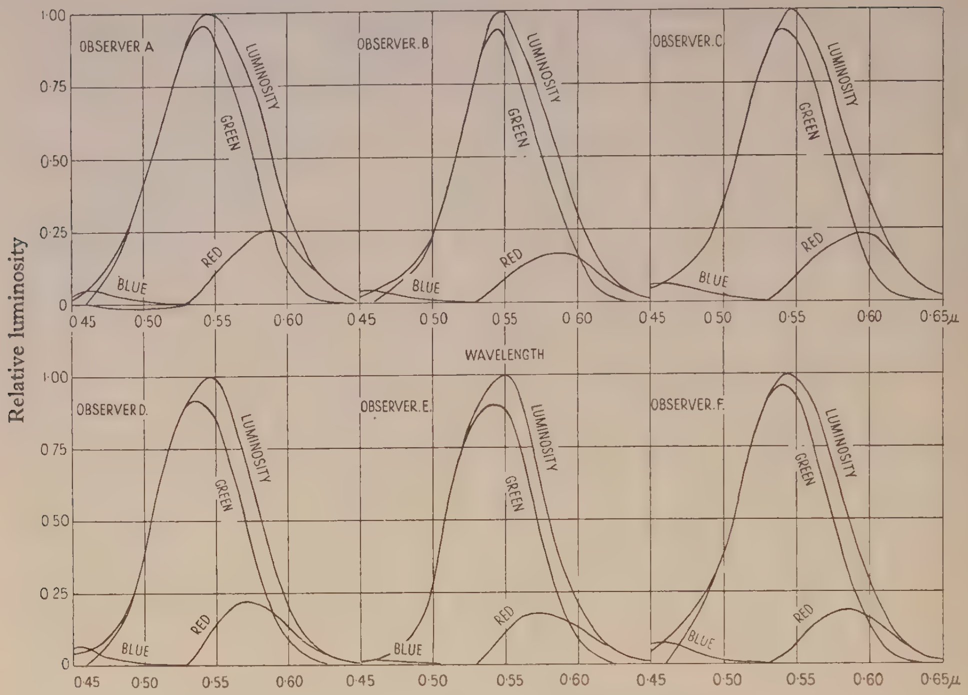

Figure 3. Luminosity and mixture curves for six protanomalous observers for an equal-energy spectrum. The reference primaries are 0·46 μ, 0·53 μ and 0·65 μ.

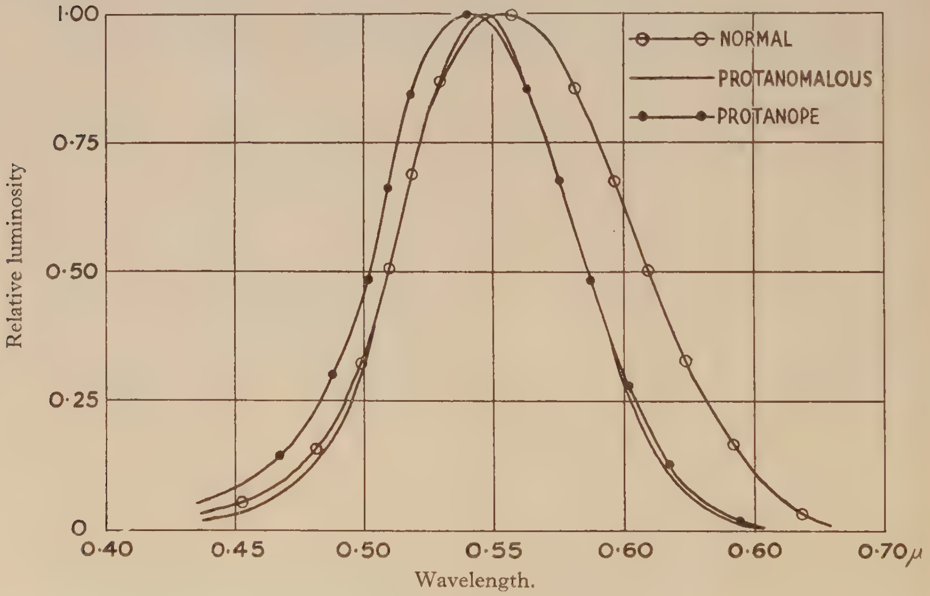

Figure 4. Luminosity curves for equal-energy spectrum for normal trichromat, for protanomalous observer and for protanope.

Table 1. Observer A

Wave-length, λ (μ)	Relative luminosity of equal-energy spectrum	Trichromatic coefficients			Mixture curves for equal-energy spectrum			Hue discrimination; just noticeable wavelength differences (μ)	Saturation discrimination $\log \frac{L_w+L_s}{L}$
		B (0·46 μ)	G (0·53 μ)	R (0·65 μ)	L_B	L_G	L_R		
0·42		1·05	−0·08	0·03					
0·43		1·04	−0·07	0·03				0·0097	
0·44		1·03	−0·05	0·02				0·0070	
0·45	0·02	1·02	−0·03	0·01				0·0050	
0·46	0·05	1·00	0·00	0·00	0·05	0·00	0·00	0·0035	
0·47	0·10	0·94	0·07	−0·01	0·04	0·07	−0·01	0·0026	1·12
0·48	0·18	0·81	0·21	−0·02	0·03	0·16	−0·01	0·0021	1·05
0·49	0·27	0·62	0·41	−0·03	0·02	0·28	−0·01	0·0018	0·97
0·50	0·40	0·38	0·65	−0·03	0·01	0·40	−0·01	0·0018	0·88
0·51	0·56	0·20	0·82	−0·02	0·01	0·56	−0·01	0·0020	0·79
0·52	0·72	0·09	0·93	−0·02	0·00	0·73	−0·01	0·0026	0·72
0·53	0·89	0·00	1·00	0·00	0·00	0·89	0·00	0·0040	0·68
0·54	1·00		0·93	0·07		0·96	0·04	0·0049	0·70
0·55	0·99		0·85	0·15		0·89	0·10	0·0049	0·75
0·56	0·92		0·77	0·23		0·77	0·15	0·0044	0·79
0·57	0·82		0·67	0·33		0·62	0·20	0·0041	0·82
0·58	0·68		0·54	0·46		0·44	0·24	0·0039	0·84
0·59	0·51		0·38	0·62		0·25	0·26	0·0041	0·87
0·60	0·33		0·25	0·75		0·11	0·22	0·0047	0·88
0·61	0·20		0·16	0·84		0·05	0·15	0·0058	0·89
0·62	0·12		0·09	0·91		0·02	0·10	0·0072	0·90
0·63	0·06		0·04	0·96		0·00	0·06	0·0085	0·91
0·64	0·02		0·02	0·98		0·00	0·02	0·0101	0·92
0·65	0·01		0·00	1·00		0·00	0·01	0·0123	0·95
Relative luminosities of primaries		0·049	1·00	0·64					

Table 2. Observer B

Wave-length, λ (μ)	Relative luminosity of equal-energy spectrum	Trichromatic coefficients			Mixture curves for equal-energy spectrum			Hue discrimination; just noticeable wavelength differences (μ)	Saturation discrimination $\log \frac{L_w+L_s}{L_s}$
		B (0·46 μ)	G (0·53 μ)	R (0·65 μ)	L_B	L_G	L_R		
0·42		1·07	−0·07						
0·43		1·07	−0·07						
0·44	0·01	1·05	−0·05		0·02	−0·01		0·0108	
0·45	0·02	1·03	−0·03		0·03	−0·01		0·0060	
0·46	0·03	1·00	0·00		0·03	0·00		0·0024	
0·47	0·07	0·91	0·09		0·03	0·04		0·0017	
0·48	0·10	0·78	0·22		0·02	0·08		0·0015	
0·49	0·14	0·60	0·40		0·01	0·13		0·0014	0·28
0·50	0·23	0·38	0·62		0·01	0·22		0·0016	0·22
0·51	0·40	0·20	0·80		0·01	0·39		0·0019	0·16
0·52	0·58	0·06	0·94		0·00	0·58		0·0027	0·13
0·53	0·78	0·00	1·00		0·00	0·78	0·00	0·0038	0·11
0·54	0·96		0·91	0·09		0·92	0·04	0·0054	0·11
0·55	0·99		0·82	0·18		0·91	0·08	0·0059	0·13
0·56	0·88		0·73	0·27		0·76	0·12	0·0053	0·16
0·57	0·76		0·64	0·36		0·61	0·15	0·0045	0·18
0·58	0·61		0·53	0·47		0·45	0·16	0·0039	0·20
0·59	0·46		0·42	0·58		0·29	0·17	0·0034	0·22
0·60	0·31		0·30	0·70		0·16	0·15	0·0032	0·24
0·61	0·19		0·20	0·80		0·07	0·12	0·0034	0·25
0·62	0·10		0·11	0·89		0·02	0·08	0·0040	
0·63	0·05		0·05	0·95		0·01	0·04	0·0050	
0·64	0·02		0·02	0·98		0·00	0·02	0·0064	
0·65	0·01		0·00	1·00		0·00	0·01	0·0082	
Relative luminosities of primaries		0·07	1·00	0·42					

Table 3. Observer C

Wave-length, λ (μ)	Relative luminosity of equal-energy spectrum	Trichromatic coefficients			Mixture curves for equal-energy spectrum			Hue-discrimination; just noticeable wavelength differences (μ)
		B (0·46 μ)	G (0·53 μ)	R (0·65 μ)	L_B	L_G	L_R	
0·42	0·01	1·05	−0·05		0·02	−0·01		
0·43	0·02	1·05	−0·05		0·04	−0·02		0·0110
0·44	0·03	1·04	−0·04		0·06	−0·03		0·0080
0·45	0·05	1·02	−0·02		0·06	−0·01		0·0053
0·46	0·07	1·00	0·00		0·07	0·00		0·0028
0·47	0·10	0·93	0·07		0·05	0·05		0·0016
0·48	0·15	0·81	0·19		0·04	0·11		0·0011
0·49	0·21	0·62	0·38		0·03	0·18		0·0010
0·50	0·34	0·38	0·62		0·02	0·32		0·0011
0·51	0·53	0·18	0·82		0·01	0·52		0·0018
0·52	0·70	0·06	0·94		0·00	0·70		0·0032
0·53	0·85	0·00	1·00		0·00	0·85	0·00	0·0049
0·54	0·96		0·94	0·06		0·93	0·03	0·0058
0·55	0·99		0·85	0·15		0·89	0·10	0·0057
0·56	0·91		0·77	0·23		0·77	0·14	0·0050
0·57	0·79		0·68	0·32		0·61	0·18	0·0042
0·58	0·61		0·54	0·46		0·41	0·20	0·0038
0·59	0·49		0·39	0·61		0·25	0·24	0·0037
0·60	0·34		0·23	0·77		0·11	0·23	0·0039
0·61	0·23		0·11	0·89		0·04	0·19	0·0047
0·62	0·14		0·06	0·94		0·01	0·13	0·0058
0·63	0·07		0·02	0·98		0·00	0·07	0·0072
0·64	0·03		0·01	0·99		0·00	0·03	0·0085
0·65	0·02		0·00	1·00		0·00	0·02	
Relative luminosities of primaries		0·075	1·00	0·63				

Table 4. Observer D

Wave-length, λ (μ)	Relative luminosity of equal-energy spectrum	Trichromatic coefficients			Mixture curves for equal-energy spectrum			Hue discrimination; just noticeable wavelength differences (μ)	Saturation discrimination $\log \frac{L_w+L_s}{L_s}$
		B (0·46 μ)	G (0·53 μ)	R (0·65 μ)	L_B	L_G	L_R		
0·42	0·01	1·00	−0·10	0·10	0·02	−0·03	0·02		
0·43	0·02	1·00	−0·10	0·10	0·03	−0·05	0·04		
0·44	0·03	1·00	−0·10	0·10	0·05	−0·08	0·06		
0·45	0·04	1·00	−0·07	0·07	0·06	−0·07	0·05	0·0060	
0·46	0·05	1·00	0·00	0·00	0·05	0·00	0·00	0·0032	
0·47	0·08	0·92	0·08		0·03	0·05		0·0018	
0·48	0·13	0·77	0·23		0·02	0·11		0·0012	
0·49	0·22	0·57	0·43		0·02	0·20		0·0009	0·25
0·50	0·38	0·33	0·67		0·01	0·37		0·0010	0·23
0·51	0·60	0·14	0·86		0·01	0·59		0·0016	0·20
0·52	0·77	0·04	0·96		0·00	0·77		0·0029	0·17
0·53	0·90	0·00	1·00		0·00	0·90	0·00	0·0044	0·15
0·54	0·98		0·90	0·10		0·91	0·07	0·0060	0·15
0·55	0·99		0·81	0·19		0·85	0·14	0·0075	0·16
0·56	0·89		0·72	0·28		0·70	0·19	0·0084	0·18
0·57	0·72		0·62	0·38		0·50	0·22	0·0085	0·20
0·58	0·53		0·52	0·48		0·32	0·21	0·0075	0·23
0·59	0·36		0·42	0·58		0·18	0·18	0·0060	0·26
0·60	0·21		0·31	0·69		0·08	0·13	0·0050	0·30
0·61	0·11		0·20	0·80		0·03	0·08	0·0057	0·34
0·62	0·06		0·11	0·89		0·01	0·05	0·0074	
0·63	0·03		0·03	0·97		0·00	0·03	0·0104	
0·64	0·01		0·01	0·99		0·00	0·01		
0·65	0·01		0·00	1·00		0·00	0·01		
Relative luminosities of primaries		0·058	1·00	0·71					

Table 5. Observer E

Wave-length, λ (μ)	Relative luminosity of equal-energy spectrum	Trichromatic coefficients			Mixture curves for equal-energy spectrum			Hue discrimination; just noticeable wavelength differences (μ)	Saturation discrimination $\log \frac{L_w+L_s}{L_s}$
		B (0·46 μ)	G (0·53 μ)	R (0·65 μ)	L_B	L_G	L_R		
0·42		1·02	−0·05	0·03					
0·43		1·03	−0·05	0·02					
0·44		1·02	−0·04	0·02					
0·45	0·01	1·02	−0·03	0·01				0·0100	
0·46	0·02	1·00	0·00	0·00	0·02	0·00		0·0050	
0·47	0·04	0·90	0·10		0·01	0·03		0·0035	
0·48	0·06	0·77	0·23		0·006	0·06		0·0029	0·70
0·49	0·13	0·57	0·43		0·005	0·12		0·0027	0·45
0·50	0·27	0·34	0·66		0·004	0·26		0·0032	0·30
0·51	0·54	0·14	0·86		0·003	0·54		0·0045	0·22
0·52	0·73	0·05	0·95		0·002	0·73		0·0064	0·21
0·53	0·86	0·00	1·00	0·00	0·000	0·86		0·0088	0·23
0·54	0·95		0·90	0·10		0·90	0·05	0·0106	0·26
0·55	1·00		0·81	0·19		0·89	0·11	0·0112	0·28
0·56	0·92		0·72	0·28		0·77	0·15	0·0105	0·24
0·57	0·73		0·63	0·37		0·56	0·17	0·0082	0·17
0·58	0·51		0·52	0·48		0·34	0·17	0·0064	0·15
0·59	0·34		0·39	0·61		0·19	0·15	0·0058	0·18
0·60	0·21		0·26	0·74		0·09	0·12	0·0076	0·22
0·61	0·12		0·15	0·85		0·03	0·09	0·0130	0·27
0·62	0·07		0·08	0·92		0·01	0·06		0·31
0·63	0·03		0·05	0·95		0·00	0·03		
0·64	0·02		0·02	0·98		0·00	0·02		
0·65	0·01		0·00	1·00		0·00	0·01		
Relative luminosities of primaries		0·03	1·00	0·52					

Table 6. Observer F

Wave-length, λ (μ)	Relative luminosity of equal-energy spectrum	Trichromatic coefficients			Mixture curves for equal-energy spectrum			Hue discrimination; just noticeable wavelength differences (μ)
		B (0·46 μ)	G (0·53 μ)	R (0·65 μ)	L_B	L_G	L_R	
0·42		1·06	−0·06					
0·43		1·06	−0·06					
0·44	0·01	1·05	−0·05		0·04	−0·03		0·0148
0·45	0·04	1·03	−0·03		0·07	−0·03		0·0115
0·46	0·07	1·00	0·00		0·07	0·00		0·0072
0·47	0·13	0·93	0·07		0·06	0·07		0·0042
0·48	0·19	0·81	0·19		0·04	0·15		0·0029
0·49	0·26	0·60	0·40		0·02	0·24		0·0020
0·50	0·39	0·38	0·62		0·02	0·37		0·0020
0·51	0·57	0·18	0·82		0·01	0·56		0·0028
0·52	0·77	0·06	0·94		0·00	0·77		0·0054
0·53	0·91	0·00	1·00	0·00	0·00	0·91	0·00	0·0086
0·54	0·99		0·95	0·05		0·97	0·02	0·0116
0·55	0·99		0·86	0·14		0·92	0·07	0·0124
0·56	0·91		0·75	0·25		0·78	0·13	0·0110
0·57	0·76		0·64	0·36		0·60	0·16	0·0093
0·58	0·60		0·52	0·48		0·41	0·19	0·0076
0·59	0·43		0·40	0·60		0·25	0·18	0·0060
0·60	0·29		0·29	0·71		0·13	0·16	0·0046
0·61	0·17		0·18	0·82		0·05	0·12	0·0041
0·62	0·09		0·08	0·92		0·01	0·08	0·0064
0·63	0·05		0·04	0·96		0·005	0·045	0·0106
0·64	0·02		0·02	0·98		0·00	0·02	0·0146
0·65	0·01		0·00	1·00		0·00	0·01	
Relative luminosities of primaries		0·069	1·00	0·48				

Table 7. Observer G

Wave-length, λ (μ)	Relative luminosity of equal-energy spectrum	Hue discrimination; just noticeable wavelength differences (μ)	Saturation discrimination $\log \frac{L_w+L_s}{L_s}$
0·42	0·01		
0·43	0·02	0·0145	
0·44	0·02	0·0095	
0·45	0·03	0·0055	
0·46	0·04	0·0035	
0·47	0·06	0·0025	
0·48	0·09	0·0018	
0·49	0·14	0·0017	0·47
0·50	0·22	0·0020	0·12
0·51	0·43	0·0030	0·04
0·52	0·69	0·0052	0·01
0·53	0·86	0·0106	0·00
0·54	0·98	0·0196	0·00
0·55	1·00	0·0280	0·00
0·56	0·88	0·0285	0·01
0·57	0·76	0·0204	0·02
0·58	0·61	0·0155	0·04
0·59	0·46	0·0137	0·07
0·60	0·32	0·0130	0·11
0·61	0·18	0·0130	
0·62	0·09	0·0138	
0·63	0·05	0·0150	
0·64	0·03	0·0164	
0·65	0·01	0·0180	

Table 8. Observer H

Wave-length, λ (μ)	Relative luminosity of equal-energy spectrum	Hue discrimination; just noticeable wavelength differences (μ)	Saturation discrimination $\log \frac{L_w+L_s}{L_s}$
0·43	0·005	0·0160	
0·44	0·01	0·0130	
0·45	0·01	0·0110	
0·46	0·02	0·0090	
0·47	0·04	0·0080	
0·48	0·10	0·0077	
0·49	0·19	0·0080	0·33
0·50	0·32	0·0103	0·22
0·51	0·48	0·0150	0·20
0·52	0·69	0·0210	0·22
0·53	0·93	0·0270	0·25
0·54	1·00	0·0310	0·26
0·55	0·98	0·0280	0·23
0·56	0·88	0·0200	0·21
0·57	0·75	0·0130	0·21
0·58	0·60	0·0093	0·22
0·59	0·41	0·0110	0·25
0·60	0·26	0·0165	0·28
0·61	0·14	0·0250	0·31
0·62	0·08	0·0360	0·33
0·63	0·04	0·0490	
0·64	0·01	0·0670	
0·65	0·01		

Table 9. Observer I

Wave-length, λ (μ)	Relative luminosity of equal-energy spectrum	Hue discrimination; just noticeable wavelength differences (μ)	Saturation discrimination $\log\frac{L_w+L_s}{L_s}$
0·45	0·01	0·0170	
0·46	0·04	0·0136	
0·47	0·07	0·0106	
0·48	0·12	0·0074	0·88
0·49	0·17	0·0048	0·50
0·50	0·29	0·0030	0·15
0·51	0·49	0·0030	0·05
0·52	0·77	0·0050	0·00
0·53	0·92	0·0093	0·00
0·54	1·00	0·0200	0·00
0·55	0·98	0·0320	0·00
0·56	0·86	0·0368	0·00
0·57	0·72	0·0360	0·00
0·58	0·57	0·0290	0·00
0·59	0·41	0·0200	0·00
0·60	0·25	0·0150	0·04
0·61	0·14	0·0122	0·10
0·62	0·07	0·0122	0·20
0·63	0·03	0·0137	
0·64	0·01	0·0160	
0·65	0·005	0·0190	

Table 10. Observer J

Wave-length, λ (μ)	Relative luminosity of equal-energy spectrum	Hue discrimination; just noticeable wavelength differences (μ)
0·43	0·005	
0·44	0·015	
0·45	0·03	0·0115
0·46	0·05	0·0090
0·47	0·08	0·0063
0·48	0·11	0·0043
0·49	0·18	0·0030
0·50	0·29	0·0029
0·51	0·47	0·0045
0·52	0·66	0·0090
0·53	0·83	0·0190
0·54	0·95	0·0310
0·55	1·00	0·0435
0·56	0·92	0·0483
0·57	0·78	0·0418
0·58	0·60	0·0292
0·59	0·43	0·0184
0·60	0·29	0·0109
0·61	0·18	0·0093
0·62	0·10	0·0112
0·63	0·06	0·0147
0·64	0·03	0·0197
0·65	0·02	0·0255

Table 11. Observer K

Wave-length, λ (μ)	Relative luminosity of equal-energy spectrum	Hue discrimination; just noticeable wavelength differences (μ)
0·44	0·005	0·0480
0·45	0·015	0·0315
0·46	0·03	0·0200
0·47	0·06	0·0100
0·48	0·10	0·0060
0·49	0·16	0·0048
0·50	0·26	0·0060
0·51	0·47	0·0100
0·52	0·72	0·0180
0·53	0·88	0·0320
0·54	0·97	0·0490
0·55	1·00	0·0638
0·56	0·92	0·0660
0·57	0·80	0·0580
0·58	0·64	0·0480
0·59	0·46	0·0450
0·60	0·31	0·0490
0·61	0·18	0·0590
0·62	0·08	0·0730
0·63	0·04	0·0870
0·64	0·03	0·1030
0·65	0·02	0·1200

§ 5. DISCUSSION OF RESULTS

It is not proposed to undertake any detailed discussion of the results in the present paper. At a later date it is hoped to prepare a comprehensive report in which the measurements on normal trichromats, both forms of anomalous trichromat and both forms of dichromat are compared and related to one another. The brief discussion that follows serves mainly to draw attention to the salient characteristics of the protanomalous observer.

The family of hue discrimination curves shows clearly how successive degrees of the defect are revealed in an increasing inability to distinguish different colours. The curves form a continuous series between the curve for the normal trichromat and that for the protanope as reported by Pitt(9). One point of special interest is that observers I and J are brothers. It is significant that they should occupy neighbouring positions in the series ; it would be of great interest to commence an investigation that aimed, in course of time, at testing several generations of families in which anomalous trichromatism occurred. It is generally recognized that the type of defect transmitted through successive generations does not change, but as the degree of deficiency has never before been completely recorded, it is impossible to say whether there is any tendency for the condition to improve or deteriorate.

The saturation discrimination curves indicate, with one exception, that the spectral colours as seen by the anomalous trichromat are less saturated than they appear to the ordinary trichromat. Moreover, there is a much smaller variation in the saturation through the spectrum, with no marked minimum in the curve at $0{\cdot}57\,\mu$. Taken in conjunction with the hue discrimination curve, it is reasonable to conclude that to the defective observer $0{\cdot}65\,\mu$ appears as a desaturated orange, and that $0{\cdot}53\,\mu$ is like a desaturated yellow-green. There is, however, no means of verifying for certain that these are in fact the sensations experienced.

The luminosity and mixture curves of figure 3 show comparatively little variation among themselves, and there is some justification for deriving a mean curve for the 11 observers. The result, illustrated in figure 4 relative to the standard luminosity curve for the trichromat and Pitt's curve for the dichromat, is very striking. On the red side of the curve there is almost perfect coincidence with the protanope curve and on the blue-green side equally good coincidence with the normal curve. In view of the wide variation among normal observers that has been found(12) at the blue end of the spectrum, the latter coincidence may only be accidental, although it is surprisingly good. In any case, the difference from the protanope curve is not very great. The coincidence between the protanomalous curve and the protanope curve, on the other hand, is much more significant, especially as the difference from the normal curve is so marked. It is difficult to reconcile this result with the usual conception that different degrees of protanomalous defect, as indicated by the hue discrimination curve, arise from the magnitude of the red response varying from one observer to another. It must, however, always be remembered that it is a purely arbitrary convention by which the maxima of different luminosity curves are raised to the same value, unity, and it may not be legitimate to compare such curves directly, if the absolute sensitivity to light is in question.

One point in connexion with the mixture curves should be mentioned. It will be noticed that, with one exception, there is no negative red in the blue-green region of the spectrum. This is somewhat unexpected, but the observers were quite satisfied with the matches they made without the introduction of any desaturating primary, so that, although some negative red should no doubt have been recorded, the amount must have been sub-liminal.

§ 6. ACKNOWLEDGEMENTS

The authors desire to express their appreciation of the financial assistance provided by the Medical Research Council for this investigation. Their thanks are also due to the observers themselves for their co-operation in the work and to the following institutions for the facilities that enabled the initial survey of the 2,000 persons to be made: the Research Laboratories of the General Electric Company, the Sir John Cass Technical Institute, the Chelsea Polytechnic, the Science Museum and the various departments of the Imperial College.

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THE PROPAGATION OF SUPERSONICS IN LIQUIDS

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ABSTRACT. By means of a hot-wire detector of amplitude, the propagation constants (of velocity and attenuation) of supersonic radiation within the range 200 to 1110 kc./sec. in water and a number of organic liquids are determined. While no dispersion of velocity is found, attenuation coefficients greater than those indicated by the Stokes-Kirchhoff formula (viscous absorption only) are obtained. Measurements of the supersonic field in front of the source do not reveal any abnormalities in the propagation of the radiation in certain organic liquids such as some other workers have claimed.

§1. SCOPE OF INVESTIGATION

Although the Pierce supersonic interferometer is as well suited to the measurement of supersonic wave-lengths in liquids as in gases, it is dangerous to deduce values of absorption coefficients from the results of such observations unless some rather uncertain precautions are taken. Some means of determining absolute amplitude is to be preferred. The means usually adopted have been either (*a*) radiation-pressure measurements, in which the amplitude at any place in the supersonic field has been deduced from the deflection of a pendulum or torsion vane, or (*b*) light-diffraction measurements, in which the absorption coefficient is deduced from the *intensity* of the diffracted images of a pencil of light cast athwart the supersonic beam. The present situation *vis-à-vis* these two alternatives can be summed up from the experience of recent workers in this field.

Biquard (1) and Grobe (4) attempt to measure the decay of amplitude of a supersonic beam in a liquid by comparing the light-diffraction patterns at various distances from the source, on the assumption that the intensity of the first diffracted image is proportional to the supersonic amplitude at the station in question. In view of the difficulties in measuring the optical intensities and the complexities in the theory of the effect, which may invalidate the assumption, it is not surprising that widely differing values for the absorption coefficient are quoted. Nor are the mechanical methods in which amplitude is measured by the pressure on a pendulum in the liquid in much better case, because the presence of a pendulum bob is found to give rise to gratuitous reflections. Probably Buss (2) has brought the technique of the pressure methods to its highest point in his work on the absorption in a stationary-wave system, since he has devised a sensitive valve circuit which embodies the pendulum as one side of a condenser. It is amusing to note that while Grobe has no faith in the pendulum method Buss condemns the optical method because he can find no connection between supersonic amplitude and diffracted light intensity.

In view of this uncertainty in the application of the two former methods, the author has relied on another, to wit, the hot-wire detector, which does not suffer from any of the disadvantages enumerated in the last paragraph. Inasmuch as Klein (7) in his recent account of the apparatus available for measuring absolute sound intensities in liquid media does not mention the hot wire, it is proposed first to give some account of the possibilities of hot-wire measurements of amplitude in sound fields in general and in supersonic fields in liquids in particular.

§ 2. THE HOT-WIRE DETECTOR OF AMPLITUDE

King (6) has derived two formulae for the rate of loss of heat per unit temperature excess from a thin wire under forced convection. Below a critical value of the velocity

$$H/\theta = 2\pi\kappa\{\log b/a\}^{-1}$$

and above this

$$H/\theta = \kappa + 2(\pi\kappa s\sigma a V)^{\frac{1}{2}},$$

where θ = temperature excess and a = radius of wire, H = heat lost per sec., κ = thermal conductivity, s = specific heat, σ = density, V = velocity of fluid and $b = \kappa\epsilon^{1-\gamma}(s\sigma V)^{-1}$, γ being the ratio of specific heats.

Thus with a given wire in a given fluid the heat loss is proportional to log V at low velocities, but eventually attains a proportionality to $V^{\frac{1}{2}}$ at higher temperatures.

In practice one works with a constant heating current (i) through the wire and measures the change of resistance (r_0 to r) or of potential (e_0 to e) across it under the action of the flow of liquid. It then appears that

$$\frac{H}{\theta} = \frac{i^2 r r_0 \delta}{r_0 - r} = \frac{i\delta}{e_0 - e},$$

δ being the coefficient of change of resistance with temperature of the wire; this is, of course, a constant for pure metals.

By putting the hot wire in the grid circuit of a valve of suitable characteristics, it is possible to obtain a linear relation between velocity (or particle amplitude in the wave) and anode current over the range required. Figure 1 shows the circuit used by the writer employing a VS 24 valve with the hot wire (HW) as grid bias, and figure 2 shows calibration curves for four of the liquids used in the present work. It will be obvious from King's second formula that the properties of the *fluid* which determine the sensitivity of the apparatus are contained in the product $\kappa s\sigma$; the greater this is, the less is the response to a given change of velocity. The appropriate values are given in the following table, together with that of air, to show that the sensitivity of the hot-wire anemometer is considerably lower in a liquid than it is in a gas. The defect may be, to a considerable extent, made up by raising the heating current, which can be done without producing such a high temperature as it would do if the wire were in air. The writer uses a thousandth of an inch nickel or platinum wire heated by a current of 0·1 amp., sufficient to raise it about 30° c. above its surroundings,

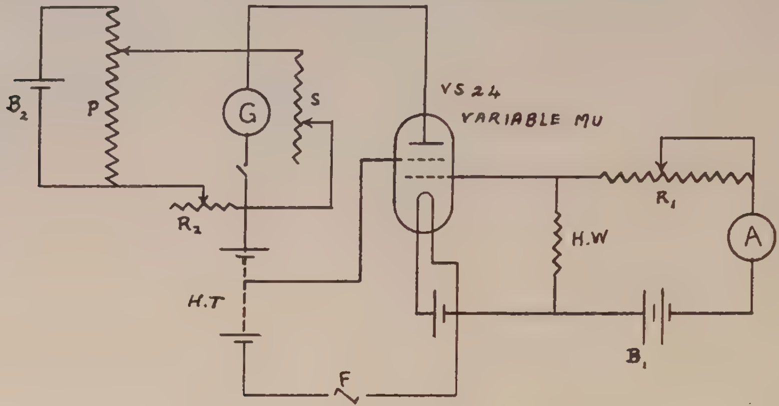

Figure 1. Amplifier for hot-wire detector.

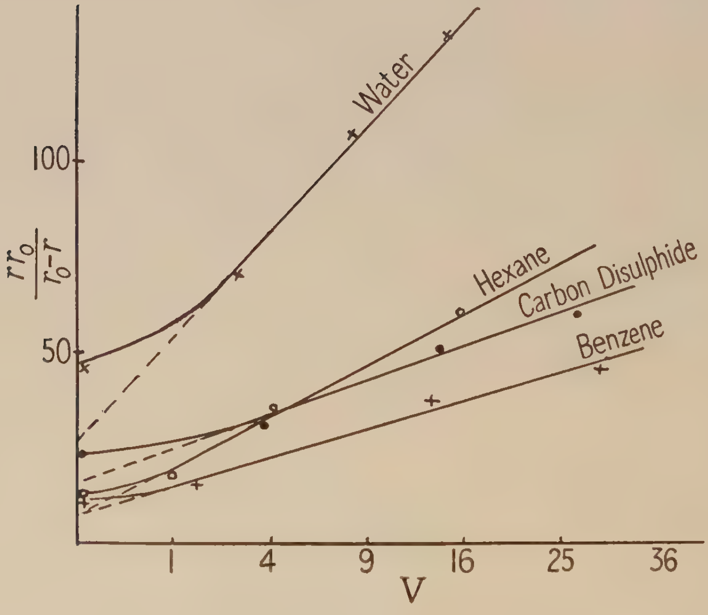

Figure 2. Calibration of hot-wire detector in liquids.

Table 1

Fluid	$10^{-4}\kappa$	s	σ	$10^{-2}\sqrt{\kappa s \sigma}$
Air	0·5	0·17	0·0013	0·011
Water	15	1	1	3·9
Hexane	4	0·50	0·87	1·3
Carbon tetrachloride	5	0·20	1·6	1·25
Carbon disulphide	9	0·23	1·3	1·1
Benzene	3·5	0·39	0·78	1

The plotted points on the calibration curves have been obtained by running the hot wire at known speeds on a small whirling arm through the liquids in question.

§ 3. APPARATUS AND RESULTS OF ABSORPTION MEASUREMENTS

The apparatus is sketched in figure 3. The quartz oscillator in the form of a disc rests on a brass plate forming the base of a glass vessel to which it is cemented, and radiates vertically. The base forms one of the electrodes. The upper one is a piece of tinfoil (" silver paper ") with which an insulated lead, passing down one side of the vessel, makes contact. The reflector, of fibre, is carried by a threaded rod, tapped to fit the cover of the vessel, carrying a graduated head on its upper end. The hot wire is mounted on the ends of two fine needles which pass through a fibre strip, also capable of fine adjustment by means of a knurled head and graduated disc on the cover. To supply the crystal a Hartley generator was used, employing a pair of T 55 valves and an anode potential of 1500 volts at 0·1 amp. The tuneable part of the circuit consisted of two Sullivan oil-filled condensers in parallel, of maximum capacity 0·001 and 0·0001 mf. respectively, and a coil allowing of tappings to give fixed inductances between 0·003 and 0·3 mh. A wave meter, guaranteed to 0·1 per cent, told when the oscillator was in resonance with the crystal. The actual supply of power to the crystal was kept as low as possible, consistent with obtaining a measurable response of the hot-wire detector, and was never sufficient to give any signs of a " mound " on the surface of the liquid, when the reflector and its support were removed from the vessel.

To prevent any radiation which had struck the walls returning to the body of the liquid an " absorbent " lining consisting of a layer of fine gauze was draped round the interior of the vessel close to the glass walls and under the lid.

Since the quartz would not oscillate under water it was placed under another liquid dielectric with a layer of distilled water above. After trying for this purpose a number of liquids having a specific acoustic impedance (= density × velocity of sound) nearly matched to that of water, nitro-toluene was found most efficacious.

To measure the wave-length of the supersonic radiation in a liquid the hot wire was set at a fixed distance (usually about 15 mm.) from the upper face of the crystal, and the reflector was moved to or from the hot wire. Maxima in the readings of the current from the hot-wire amplifying-valve also occurred at regular spacings of a half wave-length. The reflector was then fixed at an integral number of half wave-lengths from the radiating face of the crystal and the hot wire moved along a vertical traverse between them, readings being taken every fifth of a millimetre.

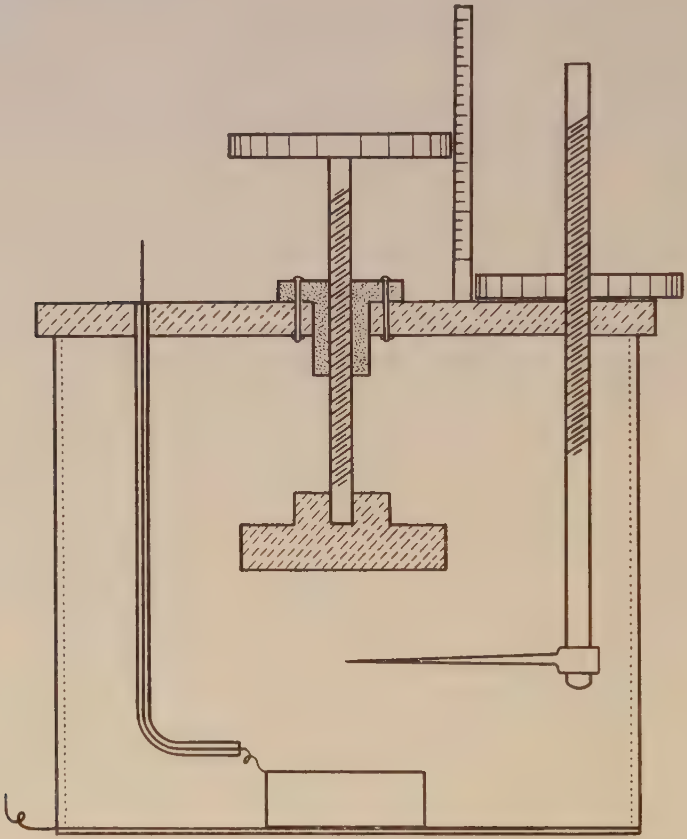

Figure 3. Hot-wire supersonic interferometer for liquids.

It has been shown elsewhere that in a stationary wave system in which attenuation is taking place with the reflector distant l from the source, the square of the amplitude at a distance x from the source is proportional to

$$\cosh [2\alpha(x-l)] - \cos [2\beta(x-l)],$$

where α is the attenuation constant and β the propagation constant $(2\pi/\lambda)$. Substituting a number of values of the square of the amplitude in the above expression for various values of x in conjunction with the value of β already determined gives the value of α.

In liquids at supersonic frequencies, α is small compared with β, so that the amplitude in the stationary wave varies between

$$\cosh\,[\alpha(x-l)] \quad \text{and} \quad \sinh\,[\alpha(x-l)]$$

multiplied by a constant representing the amplitude at the source. The values of α given in the tables are determined from these peaks and troughs in the hot-wire response.

One of the difficulties which beset all workers with supersonics in liquids is the dissipation of the heat generated, especially when, as in the present instance, most of them are bad conductors. Naturally, close watch had to be kept on the temperature of the liquid during the experiments, and in spite of stirring and thermostats, the series of measurements had frequently to be interrupted when the temperature had risen more than one degree. The rate of heating persisted while the voltage was applied to the crystal, even when the oscillator was put out of tune with the natural frequency. The author suspects that most of this rise of temperature is due to " dielectric heating " and not much to viscous absorption of the supersonics. Among the liquids used, it was greatest in nitrotoluene and least in water.

Table 2

Frequency ($10^{-5}\times$ c./sec.)	Hexane		Benzene		Carbon disulphide		Carbon tetrachloride		Water	
	$\lambda/2$	$10^5\,.\,\alpha$	$\lambda/2$	$10^5\,.\,\alpha$	$\lambda/2$	$10^5\,.\,\alpha$	$\lambda/2$	$10^5\,.\,\alpha$	$\lambda/2$	$10^5\,.\,\alpha$
2	0·30	1·75	0·31	3	0·275	1	0·24	6	0·35	2
4·65	0·13	8	0·135	15	0·118	5	0·105	30	0·155	10
6·95	0·086	20	0·0795	40	0·08	10	0·0775	75	0·103	25
10·85	0·0575	60	0·060	180	0·05	20	0·045	170	0·065	50
V (m./sec.)	1250		1250		1100		965		1440	
$10^{17}\alpha/n^2$										
expt.	50		75		20		150		50	
calc.	8		9		6		20		9	

§ 4. FORM OF SUPERSONIC FIELD

Before discussing these results, it was thought desirable to obtain some information on the form of the supersonic field in front of the quartz. For this purpose a fibre cover was placed over the quartz which left a slit 3 cm. long and of width (d) so proportioned to the wave-length of the emitted radiation that d equalled 3λ in every case. The reflector was then removed from the reservoir and the " absorbent lining " completed round the top just below the free surface of the liquid. The hot wire was mounted on the traverse belonging to a travelling microscope so that it could be set at various levels above the quartz surface and traversed horizontally in a direction perpendicular to the long side of the slit. Results at two frequencies are shown in figures 4 and 5 as plotted points on the theoretical curves for the first two or three diffraction maxima and minima from an *infinite* slit where $d=3\lambda$; α is the direction from the normal to the crystal face;

y is the height of the plane of traverse above the slit. They can be compared with the photographs of the field *in xylol* obtained by Hiedemann and Osterhammel ⁽⁵⁾, obtained by the *schlieren* method.* Of course, the comparison is not quite just, in that a slit of finite length is used in the experiments, and this may account for some of the discrepancies between theory and experiment in figures 4 and 5.

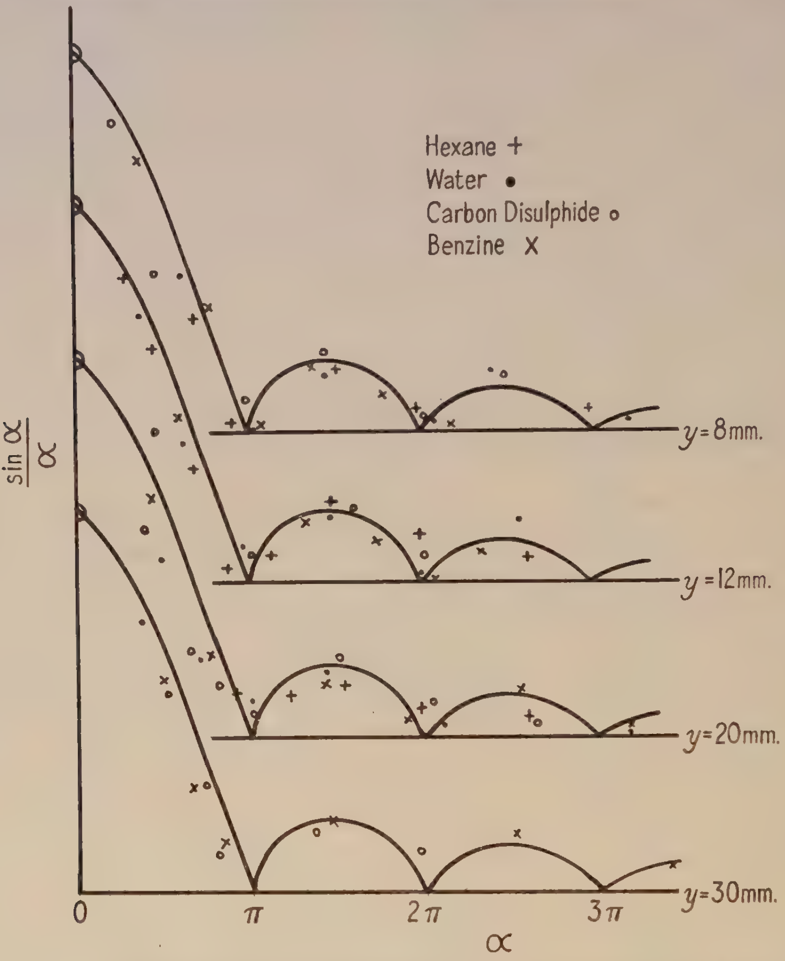

Figure 4. Supersonic field at various distances (y) in front of source of 700 kc./sec.

§ 5. DISCUSSION OF RESULTS

As we have already pointed out, there is considerable disagreement among previous workers on absorption in liquids. Claeys, Errera and Sack ⁽³⁾ ascribe some of the discrepancy to reflection from the walls of the containing vessel. Thus Sörensen ⁽¹⁰⁾ obtains a value of $\alpha = 0{\cdot}008$ in benzene at 300 kc./sec. in a tube

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* The photograph in question is reproduced in Vol. V of the *Reports on Progress in Physics*, p. 126.

8 cm. diameter, but they obtain a value one-tenth of this in a 12-cm. tube. The present value, indicated by interpolation in our table, is 0·00007, one-tenth again of the values obtained by the Belgians (and also by Biquard), but still more than eight times the Kirchhoff-Stokes' value (cf. the final rows of figures in the table).

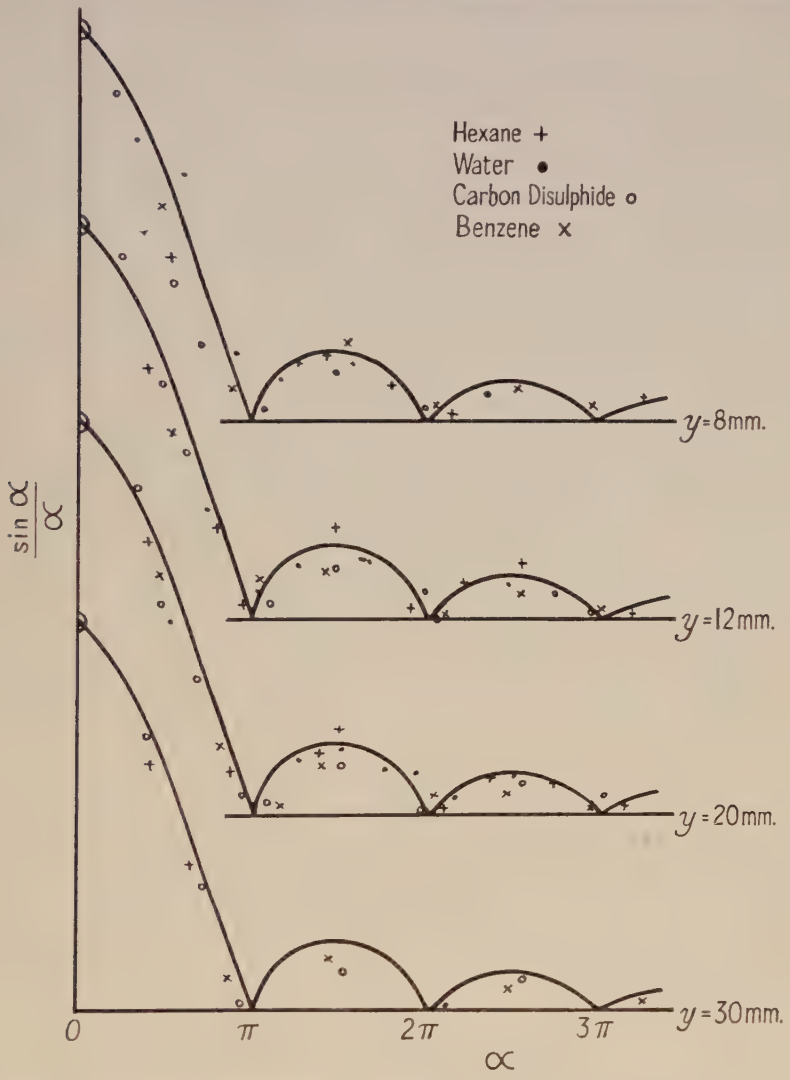

Figure 5. Supersonic field at various distances (y) in front of source of 1100 kc./sec.

Our values for water and carbon tetrachloride are in fair agreement, but again, the Belgians find enormous absorption in carbon disulphide. In spite of the fact that Claeys and his collaborators report no difference in their results as the intensity of the source was varied, the present author has found that increasing the intensity above an initial value such that turbulent motions were initiated in the liquids had the effect of enhancing the absorption severalfold. This was accompanied by an increase in the rate of heating. It was noticeably easier to do this in benzene and carbon disulphide than in water—in which it is difficult to get much power dissipation—and the present writer opines that this fact, added to the necessity for using large intensities to get a reasonable response in the pendulum device for measuring radiation pressure, accounts for the abnormal absorption found by these workers in certain liquids.

The supersonic field has been explored as described in the preceding section partly with the object of testing the hypothesis of Lucas(8), viz., that much of the supersonic radiation in benzene is scattered and not directly dissipated. Biquard in fact claims to have confirmed this by setting his radiation detector to one side of the main beam. However, one cannot say by comparing the results of the four liquids in figures 4 and 5 that there is any marked abnormality in the behaviour of benzene in this respect, though, of course, it is the natural property of all radiation debouching from an aperture which is comparable with the wavelength that some of it should be diffracted. It is probably some of this diffracted radiation, common to all fluids, which Biquard detected.

The velocity values derived from the wave-length measurements are in substantial agreement with those of Parthasarathy(9) and do not indicate dispersion with frequency, such as one would expect if scattering had supervened. It will be noticed from table 2 that though the absorption coefficients are all several times greater than the theoretical values, derived from the usual coefficient of viscosity, they occur in the same numerical order of values. Even then the experimental may be somewhat higher than the true values, when one realises that the energy represented by some of the outer diffraction bands misses the reflector and is absorbed in the walls. The same remark applies with more force to measurements with a pressure vane.

§ 6. SUMMARY

It is shown that the hot-wire detector is adapted to the study of supersonic fields in liquids and that exploration of the stationary-wave system between a supersonic radiator and a plane reflector enables one to derive values of propagation and attenuation constants for the liquids at supersonic frequencies. The values for the latter constant, though higher than those given by classical theory, do not show the excessive abnormalities reported by some previous workers.

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A SENSITIVE METHOD FOR THE DETERMINATION OF MOISTURE, APPLIED TO ELECTRICAL INSULATING MATERIALS

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ABSTRACT. A method is described for measuring the adsorbed moisture in paper, whether impregnated or unimpregnated, down to values of the order of 0·01 per cent. The essential feature of the method is the establishment of the equilibrium water-vapour pressure of the sample at a chosen temperature in a known space.

A new form of absorption apparatus is employed to measure the equilibrium water-vapour pressure, and from such measurements the original total adsorbed moisture in the sample is derived by means of a simple graphical extrapolation.

Once the relation between the equilibrium vapour pressure and the percentage of moisture has been established for a particular material, a single vapour-pressure measurement suffices to determine the moisture content of the sample. Determinations can be carried out on samples containing as little as 0·1 gramme of paper, thus making it possible to explore the distribution of moisture through the insulation wall of a high-voltage cable.

§1. INTRODUCTION

In the manufacture of insulated cables, condensers, and other electrical apparatus, paper dried to a very high standard is used as the basis of dielectric materials. In cases where only low electrical stresses occur, as in telephone cables, dry paper in the presence of dry air is employed. To extend the use of paper to the higher electrical stresses required in modern power cables, the paper is impregnated with a mineral oil, or a more viscous impregnant consisting of mineral oil to which resin or an organic polymer has been added. In order that impregnated or unimpregnated paper dielectrics shall exhibit satisfactory electrical properties, it is generally accepted that a high standard of dryness is necessary.

At the commencement of the present work, no satisfactory method was known to the authors for the measurement of minute traces of moisture in materials such as those used for electrical insulation. The need for a suitable method is mentioned by G. T. Kohman (1).

§ 2. LIMITATIONS OF THE USUAL METHODS

Many different methods are available for the determination of moisture content, but most of them depend on weighing the sample before and after drying, or on weighing the water evolved. A quartz-fibre spring-balance (2), (3), (4) may be employed for weighing the sample, and is convenient in any investigation in which a totally enclosed system is required. The drying may be done in an oven (5), or in a heated vessel under vacuum, or in a current of dry gas (6), or by distillation in an immiscible liquid (7), (8). All these methods attempt the total removal of the moisture, and the end point of the experiment is extremely difficult to determine. In actual practice, it is impossible satisfactorily to approximate to the complete removal of water from a hygroscopic substance such as paper in a reasonable time, since the rate of evolution of moisture decreases as the moisture content of the sample is reduced. The use of a very long time may lead to thermal decomposition of the sample (9), (10).

Another disadvantage of most of the well-known methods is the lack of sensitivity for very low moisture contents. The accuracy is small, since the very small loss of water has to be measured as a difference between two much larger weights. A further difficulty which may arise is the loss of non-aqueous volatiles; for example, in the case of impregnated paper, if the sample is heated under vacuum a loss of the light constituents of the impregnating oil will occur at the same time as that of the water. Extraction of the oil by means of a solvent before drying the paper is an undesirable complication and cannot easily be carried out without either gain or loss of moisture.

Many indirect electrical methods have been attempted by various workers, such as the measurement of resistivity (11), dielectric constant, dielectric-loss angle (11), and dielectric absorption. For example, Whitehead and Greenfield (12) describe a method based on the assumption that zero moisture content in cellulose corresponds to zero dielectric absorption. On this assumption the moisture content of paper samples was deduced from measurements of capacitance at high and low frequencies. All these indirect electrical methods, unfortunately, require a direct method by which to check or calibrate them.

§ 3. THEORY OF THE METHOD

The aim of the present work was to develop a sensitive and decisive method of moisture determination. The first step was to choose some property of the sample which was simply related to the percentage of moisture and which could be measured with precision. This property was found in the equilibrium water-vapour pressure exerted by the sample at a fixed temperature. By measuring the equilibrium vapour-pressure of the sample after the removal of successive measured quantities of water vapour, it is possible to plot the square root of the equilibrium vapour-pressure against the total moisture removed at each stage. With paper dielectrics, this procedure has always been found to give a straight line such as any one of those shown in figure 1. From the work of Urquhart and

Williams(13), it is clear that this simple relation is true only for the low vapour-pressure range involved in the present work. At this stage we will define zero moisture content as the state represented by the point of intersection of the extrapolated straight line in figure 1 and the abscissa. This point of intersection represents the condition of zero vapour pressure, and by definition that of zero moisture content.

It follows from the above definition that the intercept on the abscissa represents the total initial moisture in the sample. The total moisture as defined above clearly has a real physical significance, since the straight-line law observed becomes a particular case of the well-known Freundlich isotherm(14),(15)

$$m/M = Kp^{1/n}.$$

In this equation, m/M is the proportion by weight of the adsorbed vapour, and K and n are constants for each particular case if the temperature is constant. It is clear that the total moisture as defined by the authors is the adsorbed moisture to which the Freundlich isotherm refers.

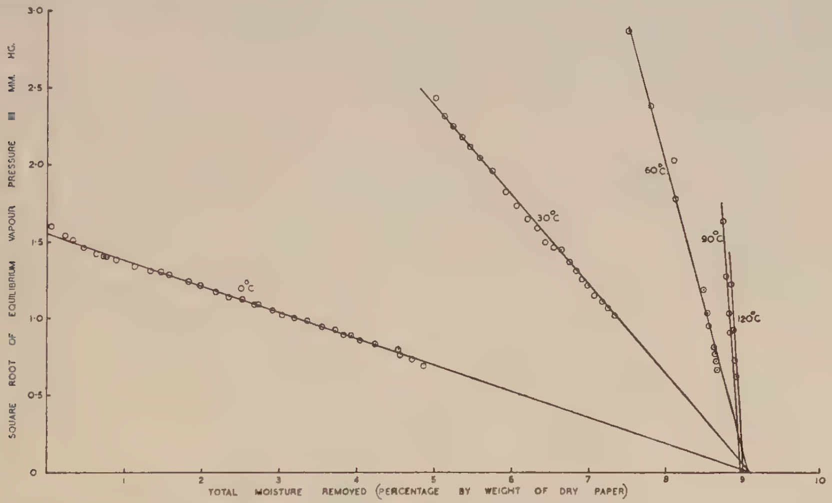

Figure 1. Relation between equilibrium vapour pressure and moisture removed for unimpregnated paper at different temperatures.

The physical significance and practical value of the authors' definition of total moisture is further demonstrated by the fact that the total moisture as defined is independent of the temperature at which the determination is made. This is illustrated by the results plotted in figure 1, which were obtained on a sample of unimpregnated wood-pulp cable-paper. The procedure, described in detail later, of establishing successive equilibrium values of the water-vapour pressure after the absorption of known quantities of vapour, was adopted. The experiment was commenced with the sample maintained at 0° c. After a number of readings had been taken, the temperature was raised to 30° c. and further equilibria established. The temperature of the sample was then raised successively to 60° c., 90° c., and 120° c., similar readings of equilibrium vapour-pressure being made at each temperature. It will be seen that the relation between the square root of the equilibrium vapour-pressure and the mass of water vapour adsorbed from the sample at each stage is approximately a straight line for each of the temperatures used between 0° c. and 120° c. It will be seen also that, within the limits of experimental error, all the straight lines when extrapolated indicate that the original percentage of moisture was 9·0. This result indicates that all the moisture in the paper which contributes to the vapour-pressure at any one temperature also contributes its appropriate share of the total vapour-pressure at any other temperature. There was, therefore, no moisture in the sample which could be regarded as in a latent or inactive state at the lower temperatures.

The above results show clearly that the temperature at which the determination is made does not affect the results, presuming, of course, that the substance under test is chemically stable at the temperature employed.

§ 4. APPARATUS

The apparatus is shown in figure 2, and consists essentially of a device for measuring the equilibrium water-vapour pressure exerted by the sample, which is placed in the side tube on the left. The two globes A and B are each of about 400 c.c. capacity, and are connected by a manometer containing Apiezon oil.

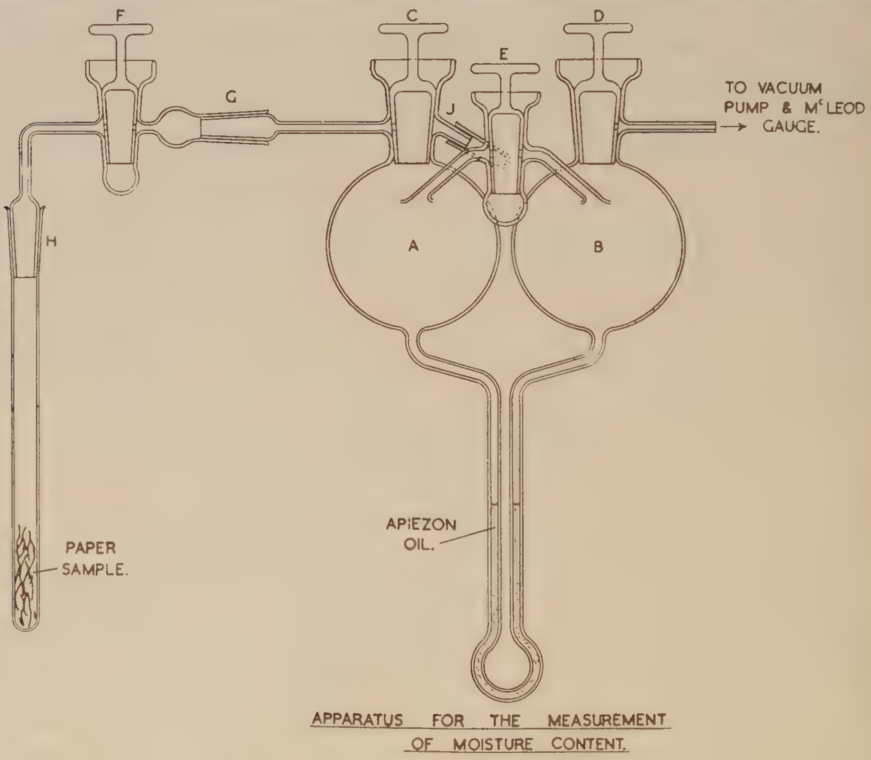
F
C
D
E
G
J
TO VACUUM PUMP & M^c LEOD → GAUGE.
H
A
B
APIEZON OIL.
PAPER SAMPLE.
APPARATUS FOR THE MEASUREMENT OF MOISTURE CONTENT.

Figure 2.

Each globe is surmounted by a ground-glass tap, and they are also connected by another tap E. Globe A is connected through its tap to a standard ground-glass joint G. This leads by another tap F to another ground-glass joint H to which the tube containing the sample is connected. The tap above globe A has a small removable side tube J connected to it. This side tube contains phosphorus pentoxide. The whole apparatus can be evacuated through the tap D by means of a rotary oil vacuum pump.

The measurement of the equilibrium water-vapour pressure is carried out at a low air pressure of less than 0·1 mm. Hg. The evacuation of the sample is done without sensible loss of moisture by cooling the sample to about −80° c. in a freezing mixture of solid carbon dioxide and alcohol. The equilibrium water-vapour pressure is built up and measured while the sample is kept at 120° c. in an oil bath thermostatically controlled to within 1° c.

When the equilibrium vapour-pressure has been built up in the globe A, the difference in level of the oil manometer is read. The tap C is then turned so that the P_2O_5 in J is exposed to the globe A. The water-vapour pressure in the globe is thus reduced to a negligibly small value(16). When the pressure is again constant, the oil manometer is read and the difference between the readings before and after absorption gives the value of the equilibrium water-vapour pressure.

§ 5. PREPARATION OF THE SAMPLE

When carrying out measurements on paper which has been impregnated with a mineral oil, it is essential to use thin samples consisting of a short piece of a single paper strip. If thick samples are used consisting of several closely packed layers of paper, the time taken to establish equilibrium is very long. This happens because the transfer of moisture between the paper layers is very slow. The samples which are usually examined contain from 100 to 500 milligrammes of dry paper after extraction of the impregnant. With a typical moisture content of 0·1 per cent the total moisture contained in a sample may be only 0·1 of a milligramme. In measuring quantities of this order, great care is necessary to avoid contamination of the sample in handling. The sample tube in which it is placed must also be very carefully dried. This is usually done by placing it in position on the apparatus and evacuating it while hot. While still under vacuum, the tap F is shut and the tube and tap detached at the ground joint G and placed in a box containing dry air in which the cable sample is dissected. This procedure is necessary, since the amount of moisture contained in the volume of atmospheric air in the sample tube would be an appreciable percentage of the moisture contained in the sample, and the cooling before evacuation would cause this atmospheric moisture to be retained on the sides of the tube and thus introduce an error into the measurement.

Measurements are usually carried out on 3-inch lengths cut from the cable to be examined. These are stored until required in carefully dried glass jars having ground-glass stoppers rendered air-tight with rubber grease. When ready for a test, the lead sheath is split open by means of a jointer's knife and hammer, removed, and the sample returned to its jar.

The jar containing the sample is then placed inside the dry-air chamber; this consists of a wooden box with a closely fitting lid having a glass window in it. The interior of the box is treated with a non-hygroscopic paint (a vacuum lacquer containing chlorinated rubber has been found suitable). The box has two hand holes, each about 4-inches diameter, cut in one side. Rubber gauntlet gloves are fitted over short pieces of brass tubing which project into the box from these holes. By placing the hands inside these gloves, manipulations can be carried out inside the box without the presence of the worker moistening the air inside.

The box is provided with a perforated zinc tray under which are placed dishes containing P_2O_5; thus all handling is carried out in the closed box in an atmosphere of dry air. The actual strip of paper which is selected for test is always handled with tweezers. There is little risk of appreciable gain or loss of moisture with impregnated paper under these conditions. The ends of the strip are cut off with scissors before placing it in the sample tube; this reduces to a minimum the possibility of error due to moisture having been absorbed by exposure of the cut ends of the cable sample to the atmosphere.

The previously dried and evacuated sample tube should be ready inside the box. The tap F is turned to admit dry air to the sample tube, the tap unit removed, and the sample placed inside the tube by means of tweezers. The tap unit is then replaced and the tap F closed. The sample tube may then be removed from the box and attached to the absorption apparatus. By these means dry air only is admitted to the sample tube.

§ 6. MEASUREMENT OF THE EQUILIBRIUM WATER-VAPOUR PRESSURE

After immersion of the sample tube for 15 minutes in a mixture of solid CO_2 and alcohol contained in a vacuum flask, the tap F is opened to connect the sample to the already evacuated apparatus, and the absolute pressure throughout pumped down to a value not exceeding 0·1 mm. Hg. The appropriate taps are then turned to leave the sample to build up its equilibrium vapour-pressure in globe A. The establishment of the equilibrium vapour-pressure in globe A can be observed from the indication of the oil manometer. A typical set of observations is graphed in figure 3. A standard time of 1 hour is usually allowed for building up. Provided a standard procedure is adopted, it is not essential to reach perfect equilibrium, the "one-hour value" being an equally useful function of the moisture content for the purpose of extrapolation. At the end of the standard building-up period, the water-vapour pressure in globe A is calculated from the difference between the readings before and after absorption. Knowing the volume of globe A and the atmospheric temperature at the time of absorption, the mass of water absorbed may also be calculated. The tap C is then turned to re-connect the sample to the globe, and the vapour-pressure is again allowed to build up. This procedure is repeated at least three times, so that three or more points are available on the graph for extrapolation to obtain the total initial miosture. This is usually expressed as a percentage of the mass of dry paper in the sample, which is determined at the end of the test by weighing the sample after extracting the impregnant with an organic solvent.

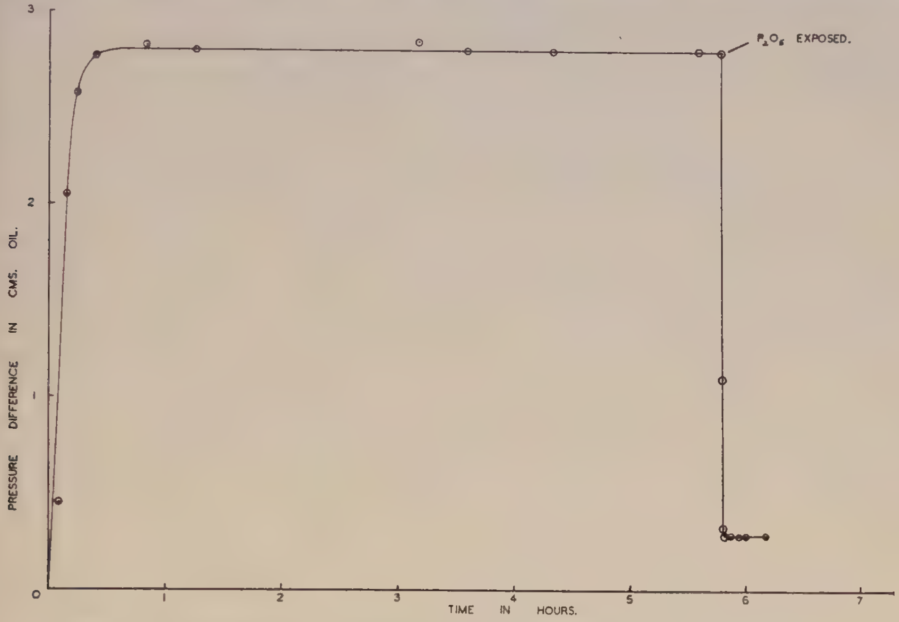

Figure 3. Building up of equilibrium vapour-pressure and absorption by P_2O_5.

§ 7. DETERMINATION OF THE TOTAL MOISTURE FROM THE VAPOUR-PRESSURE MEASUREMENTS

The method of plotting the results for any sample of impregnated paper to obtain the total moisture content is best described by an example. Table 1 gives the results obtained from a series of equilibrium vapour-pressure measurements on a sample of impregnated paper.

Column 1 gives the equilibrium vapour-pressure in mm. of mercury, while column 2 gives the square root of this value. The air temperature at each measurement is shown in column 3. The amount of moisture in the space above the sample and the amount absorbed in the globe A at each equilibrium are calculated from the known density of water vapour$^{(17)}$. In calculating the amount of moisture in the space it can be assumed that the whole space is at atmospheric temperature; part of the sample tube is actually at 120° c., but the volume of this is small compared with the volume of globe A, and the difference in temperature can be neglected. Column 4 gives the amount of moisture in the total space at each state of equilibrium. Column 5 gives the amount absorbed from globe A in each pressure measurement. Column 6 gives the total amount absorbed in all previous measurements prior to the establishment of each equilibrium vapour-pressure. Column 7 gives the total amount of moisture evolved from the sample when each equilibrium had been established. This is the quantity which must be plotted against the square root of the equilibrium vapour-pressure. It will be seen from the table that for the first equilibrium vapour-pressure this quantity is equal to the amount of water in the space. For the second equilibrium vapour-pressure it is given by the amount of water previously absorbed plus the amount in the space at the second equilibrium vapour-pressure, and so on.

Table 1

1	2	3	4	5	6	7
Equilibrium vapour-pressure (mm. Hg)	Square root of equilibrium pressure	Atmospheric temperature (° c.)	Moisture in the space (389 c.c.)	Moisture absorbed from globe A (342 c.c.)	Total moisture absorbed before equilibrium	Total moisture evolved before each equilibrium
8·38	2·90	19·8	4·210	2·820	—	3·210
2·345	1·53	23·0	0·890	0·784	2·820	3·710
0·884	0·94	14·8	0·345	0·303	3·604	3·949
0·308	0·56	20·7	0·118	0·103	3·907	4·025

Weight of dry paper=0·400 gm.

These results are plotted in figure 4. From this graph it will be seen that by extrapolation to zero equilibrium vapour-pressure, the initial moisture in the sample was 4·26 milligrammes. The mass of dry paper in the sample was 0·400 gm., so that the initial moisture content was 1·06 per cent.

§ 8. A SHORTER METHOD REQUIRING ONLY A SINGLE EQUILIBRIUM VAPOUR-PRESSURE MEASUREMENT

From a graph such as that shown in figure 1 it is possible to determine the relation between the square root of the equilibrium water-vapour pressure and the moisture content of the sample. If this relation is the same for all similar samples of paper, it is possible to determine a moisture content by means of a single equlibrium vapour-pressure measurement.

Having measured the equilibrium vapour-pressure in the manner just described, this relation will at once give the moisture content of the sample as it is in the apparatus after establishing the equilibrium vapour-pressure. From the measured vapour-pressure the amount of moisture which has been given off by the sample in building up this vapour-pressure must be calculated, knowing the volume in which it is built up. This moisture must then be added to the moisture content of the sample just determined to obtain the initial moisture-content. By this method, a moisture-content determination can be carried out in a much shorter time; actually a complete determination by this method takes about two hours, and the observer's whole attention is required only for about half of this time.

Determinations of the complete isotherm on a large number of impregnated paper samples have shown that the relation between the moisture content and the square root of the equilibrium vapour-pressure does vary to some extent among samples similar in paper and impregnating liquid. Fortunately, this variation does not seriously affect the accuracy of the results obtained by the short method. This is due to the fact that with the small samples of impregnated paper which are used most of the moisture is given off into the space in building up the first equilibrium pressure. Since the calculation of the amount of moisture in the space is obviously independent of any knowledge of the isotherm, variations in the latter do not produce such a serious effect on the total moisture content as might be expected. For instance, in the measurement, the results of which have already been quoted in table 1, the total moisture content as given by the graph in figure 4 was 1·06 per cent and the value of *K* in the Freundlich equation was 0·09. The mean value of the constant *K* as determined from a large number of graphs for different papers and impregnants is 0·05, i.e., an equilibrium vapour-pressure of 1 mm. Hg corresponds to a moisture content of 0·05 per cent at 120° c. If we use this value to calculate the moisture content of this particular sample from the first equilibrium pressure which was established, the moisture content derived would have been 0·95 per cent instead of 1·06 per cent. The

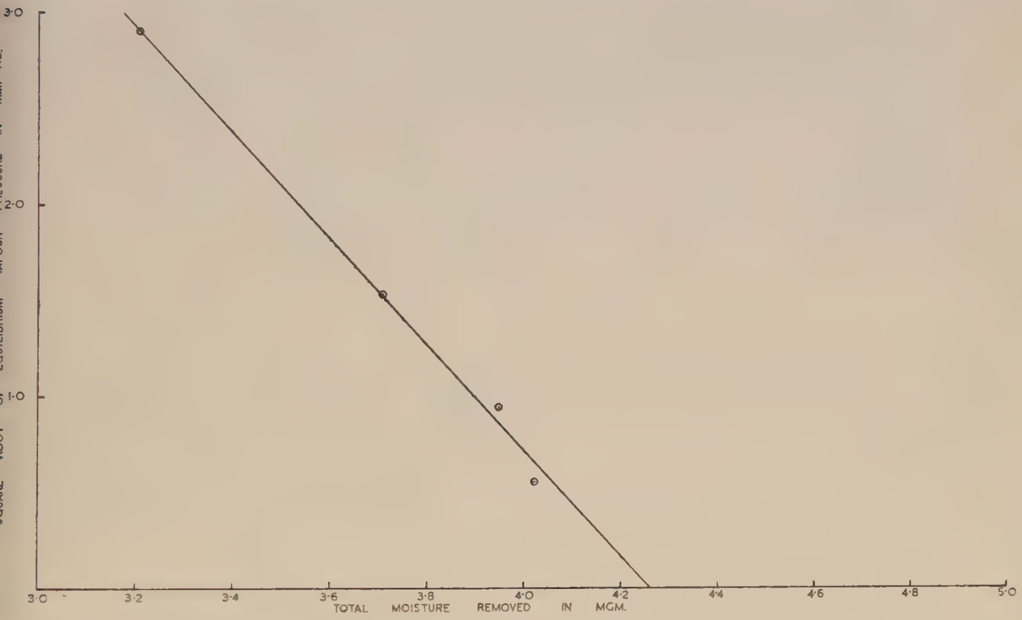

Figure 4. Relation between equilibrium vapour-pressure and total moisture removed for impregnated paper at 120° c.

agreement between these two values is quite close, although the constant K in this extreme case differs from the mean value by 80 per cent.

It was realized that in both the short and the long method any adsorption of moisture on the walls of the apparatus would introduce an error into all calculations of mass of desorbed moisture. Experiments carried out to estimate the magnitude of this error showed it to be small and consistent throughout the work. For investigations which are primarily qualitative in nature, it has been considered unnecessary to make corrections for adsorption on the glass.

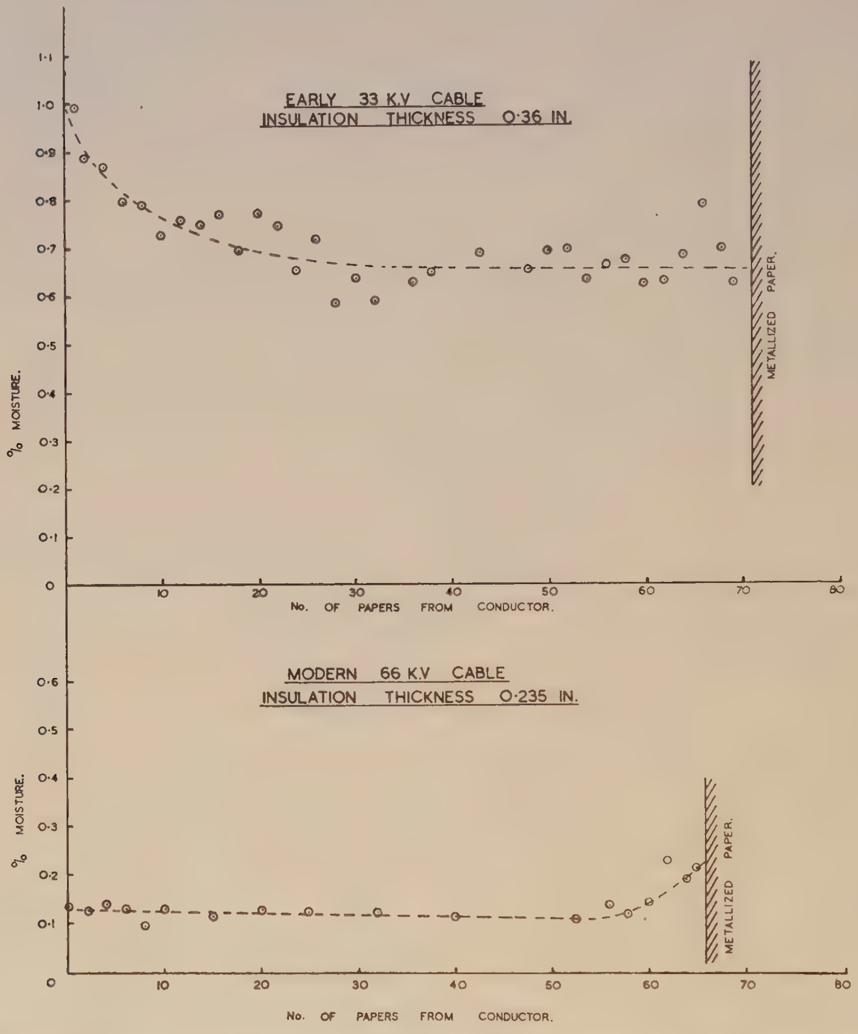

Figure 5. Moisture content distributions through the dielectrics of two high-voltage cables.

§ 9. SOME EXAMPLES OF THE USE OF THE NEW METHOD OF EXAMINING THE MOISTURE DISTRIBUTION IN POWER CABLES

The method of determination of moisture already described permits determinations to be carried out on such small samples that a single strip of paper 10 cm. long by 2 cm. wide is sufficient for a test. This enables the distribution curve for moisture through the dielectric wall of a high-voltage cable to be explored. Such a set of results is shown graphically in the lower curve of figure 5 for a 66-kilovolt impregnated gas-pressure cable which was manufactured by modern processes and method of control. Separate vacuum-drying and impregnating processes were employed, the absolute pressure prior to impregnation being 0·1 mm. Hg. The upper curve shows a similar set of results for a 33-kilovolt cable manufactured many years ago by a combined drying and impregnating process which was then almost universal practice. The method employed at that time was to boil out the moisture while the cable was immersed in the impregnating compound with a rough vacuum over the surface.

These two examples have been chosen to illustrate the application of the method to the study of the manufacture and performance of high-voltage cables. The authors hope that the method will be found useful for many other purposes and applicable to a great variety of materials.

ACKNOWLEDGEMENT

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THE SCATTERING OF D-D NEUTRONS

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ABSTRACT. The scattering cross-sections for the combined processes of absorption and inelastic scattering of D–D neutrons have been measured in 24 elements. Phosphorus, in which the 170-min. period of ^{31}Si was induced, was used to detect the neutrons, which had an energy of 3·25 Mev. The results obtained corroborate the conclusions of Kikuchi and Aoki; the cross-section does not increase monotonically with atomic number, but rather shows a periodic dependence on atomic number.

Using phosphorus as detector (threshold excitation energy about 2 Mev.), it was not possible to observe elastic scattering of D–D neutrons.

§ 1. INTRODUCTION

Experiments hitherto performed on the scattering of fast neutrons can be divided into three classes according as the neutron source employed is a Rn–Be source, a photo-neutron source, or a D–D source. Dunning's (1) work on the Rn-Be source, using good geometry and employing a paraffin-lined ionisation chamber as detector, yielded results suggesting that the (absorption + total scattering) cross-sections of elements for fast neutrons increase with atomic number in roughly the manner to be expected from classical considerations, i.e. the cross-section varies approximately as $Z^{2/3}$. Experiments with neutrons of medium energy, such as those produced by the action of the gamma rays of radium on beryllium, with an average energy of ½ Mev., show no such concordance (2). The cross-sections may differ from each other by factors of as much as 50, and there is no apparent general increase of cross-section with atomic number: the cross-section of magnesium, for example, is large, that of gold is small, and that of thallium is almost zero.

Neither investigations with the Rn–Be source nor with the photo-neutron source allow the possibility of determining resonance levels of the elements for fast neutrons; to investigate such levels a monochromatic source of neutrons such as the D–D source must be used. The first experiments on the total collision (capture + scattering) cross-sections of elements for D–D neutrons were performed by Kikuchi and Aoki (3), who used, as detector, first a counter surrounded by cadmium (the neutrons from the target having been slowed down by paraffin), and subsequently an ionisation chamber containing methane under pressure. Their results showed that, while the cross-section did increase with atomic number, there were local variations which suggested a periodic dependence of cross-section on atomic number. Thus, there were minima of cross-section for oxygen ($Z=8$), sulphur ($Z=16$), titanium ($Z=24$) and in the neighbourhood of the zinc-copper group. If this is the case, it is both interesting and important. Analogous work by Zinn, Seely and Cohen(4) in which a helium-filled ionisation chamber was used as detector did not confirm the periodic relation suggested by the results of Kikuchi and Aoki ; it is true that the variation of the total cross-section from element to element was not haphazard, but the relation between the various cross-sections did not appear to be that of a simple period. The observations of Zinn, Seely and Cohen are open to the criticism that they were made cyclically; a D–D source is not usually so constant as to allow such observations to be strictly accurate.

The theoretical investigation of the problem is little developed. According to the many-body treatment of the nucleus, the number of levels in the nucleus should increase with increasing atomic weight and increasing excitation energy up to a limit of about 20 Mev. The detailed investigation of the behaviour of scattering cross-section with atomic number has been undertaken by Fay(5), using the Van Vleck potential to simplify the model of the nucleus. His results definitely predict the existence of resonances for certain elements, but these are less frequent and more marked than the results of Kikuchi and Aoki suggest.

All observers of scattering cross-sections of elements for fast neutrons have employed detectors which are sensitive to an unspecified range of energy of the incident neutrons. Thus if elements such as aluminium, silicon or iron are used, the threshold excitation energy is determined only very roughly by calculation ; if ionisation chambers are employed and observations made on the recoiling protons or helium nuclei, then again it is difficult to determine the exact range of neutron energy to which the detector is sensitive. In the experiments to be described below, phosphorus, in which the 170-min. period of ^{31}Si was induced, was used as detector for the neutrons of energy 3·25 Mev. from the D–D reaction. It is advantageous to use this element because its threshold energy of excitation is in all probability not less than 2 Mev. Because of this, however, the element is not strongly activated by D–D neutrons, with the result that the detector has to be placed near the source and the geometry is not good. The values of the cross-sections observed (absorption + inelastic scattering) are of the same order as those found by investigators using elements as detectors, but are only about half the values obtained by workers using ionisation chambers and amplifiers. The trend of cross-section with atomic number definitely confirms the results obtained by Kikuchi and Aoki, suggesting almost a periodic variation of cross-section with atomic number. A table of the results obtained, compared with those of other investigators, is given at the end of this paper, together with a graph of the results as compared with those of Kikuchi and Aoki.

§ 2. APPARATUS

The apparatus used was similar to that described by Booth and Hurst⁽⁶⁾. Deuterons produced by a low-voltage arc, carrying 1 amp. at about 150 v., were accelerated by a single stage of 320 kv., and focussed on to a heavy-ice target, cooled by liquid air. The equivalent source-strength of the neutron beam was about 3 curies of Rn–Be neutrons. Observations were made on the neutron beam proceeding from the target in a direction coaxial with the incident deuteron beam, since (*a*) this beam has greater intensity and energy than a beam proceeding at an angle to the incident deuteron beam, (*b*) any errors arising from a change in the focussing or position of the target are then of the second order, and may be neglected, and (*c*) there is negligible variation in energy and intensity due to poor geometry of the experimental arrangement. The liquid air cooling the heavy-ice target was contained in a 2-litre cylindrical vessel surrounding the scattering substance and detectors.

The red phosphorus used as a detector was weighed out into packets with a double lining of cellophane and aluminium. These deteriorated after two or three months, but it was found possible to make up sets of packets so nearly identical that the activities induced in them by a given neutron beam were equal to within experimental error. The packets after activation were wrapped around an electron counter and the activity was recorded by an amplifier-thyratron circuit. At first a single-stage amplifier was employed, but later, when it was necessary to count activities of upwards of 1000 per min., a Wynn-Williams scale-of-four unit was used. A check was kept on the residual liquid air at the end of each irradiation; as no systematic variation of the results with the amount of residual liquid air was observed, it was concluded that any possible effect of elastic scattering of the neutrons by the liquid air was negligible.

§ 3. THE THRESHOLD EXCITATION ENERGY OF PHOSPHORUS, AND THE HALF-LIFE PERIOD OF ^{31}Si

Two facts suggest that the threshold excitation energy of phosphorus is about 2 Mev. :—

(1) In his experiments on the variation of cross-section of phosphorus as the energy of the neutrons is varied between 2·1 and 3·0 Mev., Aoki⁽⁷⁾ has observed that there is a pronounced minimum in the total cross-section when the incident neutron energy is 2·25 Mev. A possible explanation of this phenonemon is that at and above an excitation energy of 2·25 Mev. the nucleus is able to emit protons as well as neutrons, so that, from that point onwards, the effective cross-section increases rapidly.

(2) Our experiments have shown that elastic scattering by iron of neutrons of energy 3·25 Mev. cannot be observed by using phosphorus as a detector. The experiments of Grahame and Seaborg⁽⁸⁾ have shown that it is easily possible to observe quasi-elastic scattering of Rn–Be neutrons by using as detectors strips of iron, which by rough calculation are not activated by neutrons of energy less than about 7 Mev.: the degree of elastic scattering without any very elaborate

experimental arrangement amounted to 25 per cent. The maximum energy of the Rn–Be neutrons is 13·7 Mev., although their average energy is in the region of 5 Mev. If, therefore, the threshold energy of phosphorus is 1·7 Mev. or lower, it should have been easily possible to detect elastic scattering of neutrons of uniform energy 3·25 Mev.; the fact that it was impossible to do so again suggests that the threshold energy must be well above 1·7 Mev.

In the course of our work, the half-life period of radioactive silicon, which has been variously given as 2·4 hours and 170 min., was measured. Our results all showed that 170 min. was the more accurate figure for the value of the half-life.

§ 4. THE ELASTIC SCATTERING OF FAST NEUTRONS

The degree to which the interaction of fast neutrons with nuclei results in (i) the elastic scattering, (ii) the inelastic scattering, or (iii) the absorption of the neutrons has been studied by various investigators. Dunning, Pegram, Fink and Mitchell(9) concluded that 90 per cent of the collisions were elastic, i.e. the neutron was re-emitted with roughly the same energy as its initial energy. However, both their experimental arrangement and their calculation are somewhat doubtful. A similar result was given by Aoki(10), who compared his values of the cross-sections for the neutrons, as given by the gamma rays emitted by the element when bombarded with neutrons, with the values given by Dunning(1). Since, however, in the course of his calculations Aoki had to make an estimate of the number of neutrons emitted by his source, as well as of the efficiency of his counter, his results are likewise open to criticism. Accurate work on the subject was done by Seaborg, Gibson and Grahame(11), who showed that fast neutrons are little absorbed by nuclei, but that in the course of their passage through matter there is a considerable degree of retardation. Subsequently Grahame and Seaborg(8) showed that there was an observable degree of quasi-elastic scattering from iron. Two iron targets (composed of thin strips stacked together), equidistant from the source, were shielded from it by the same length of iron, but one target was shielded by a much greater width. The activity induced in the latter was 25 per cent greater than that induced in the former, and the difference can be attributed only to elastic scattering in the iron. Curiously enough, an experiment which should have been much more sensitive to this effect, partly because of a better arrangement, partly because foils of aluminium were used as detectors (the threshold energy of aluminium is given by calculation as about 4 Mev.), gave an apparent increase due to elastic scattering of only 4 per cent.

To interpret our observations on scattering cross-sections of elements for D–D neutrons, it was essential to know the degree of elastic scattering of fast neutrons from nuclei. Experiments were first conducted to observe the back-scattering of Rn–Be neutrons from potassium dichromate crystals, since these contained elements which represented a good range of atomic weights. The scattering was measured, first from a plane face of the crystals, the scattering depth being 2·5 cm., and then from crystals in a tube, the phosphorus detector packets being wrapped round the tube. Within the limits of experimental error, there was no observable elastic scattering. In case this null effect was due to the small concentration of the substance under observation, the experiment was repeated on a 20-lb. block of lead. Again it was not possible to observe effects due to elastic scattering. A check experiment using an iodoform detector, which is more sensitive to slow neutrons, gave, as was to be expected, an increase in activity of 40 per cent on bringing up the lead block. Using a phosphorus indicator, a back-scattering experiment was then carried out with a smaller volume of iron, and the resulting increase of activity (16 per cent) was much greater than the statistical errors involved (3 per cent). It is true that the concentration of iron atoms is about 3 times as great as that of lead atoms ; but the cross-section of lead for fast neutrons is about twice as great as that of iron, so that, the rest being equal, the effect of elastic scattering might be expected to be only 50 per cent greater in the case of iron. Our results, however, show that the elastic scattering of Rn–Be neutrons, using a phosphorus indicator, is definitely observable in the case of iron, while it is not observable in lead. Thus, our experiments confirm those of Grahame and Seaborg(8) on the quasi-elastic scattering of Rn–Be neutrons from iron. The results also bear out theories of the nucleus such as those developed by Weisskopf(12), according to which the density of levels of a nucleus increases with increasing atomic number. The lead nucleus should have a greater number of levels than the iron nucleus, and in particular a greater number of levels below 1 Mev. Hence the probability of emission of a gamma ray during the period of excitation should be greater in the case of lead and the degree of elastic scattering proportionally less.

Since the elastic scattering of Rn–Be neutrons was not easy to observe, it was not likely that it would be observable in the case of D–D neutrons, again using phosphorus as detector. This was, in fact, the case. Two sets of phosphorus packets were placed at distances of 4 and 9 cm., respectively, from the heavy-ice target, and the ratio of their activities was measured. Behind the distant packet—i.e. on the side remote from the target—was next placed, in two experiments a block of 150 gm. of sulphur, in a third experiment a block of 1500 gm. of iron. Any elastic scattering of D–D neutrons from these blocks should give a greater relative increase in activity of the packet nearer to them. The total probable statistical error involved in the comparison of the ratios was about 4 per cent; but the ratios of the scattered and the unscattered activities, both in the case of sulphur and in the case of iron, agreed to within 2 per cent. Hence the effect of elastic scattering was quite unobservable with a D–D source and phosphorus detectors.

§ 5. THE MEASUREMENT OF D–D CROSS-SECTIONS

Even though our attempts to observe the elastic scattering of D–D neutrons had met with negative results, care was taken to design the geometry of the scattering experiments proper in such a way as to minimise any possible effects of elastic scattering. During an irradiation, lasting for 30 min., two phosphorus detector packets were employed, the one placed 4 cm., the other placed 9 cm., above the target. The first packet served as a gauge of the total neutron intensity emitted from the target, while the second determined the degree of scattering. The ratio of the two activities gave the degree of transmission corrected for variations in intensity of the neutron beam. Experiments were carried out in turn with and without the presence of a 5-cm. length of scattering substance between the packets. The geometry of the target relative to scatterer and detectors is shown in figure 1.

A table of the results obtained for the various elements investigated, together with an estimate of the error involved, is given below. In each case the value given for the cross-section for the combined processes of absorption and inelastic scattering is the mean of at least three actual determinations. The estimate of the error is based on a statistical procedure; the figure given is the maximum probable deviation of the actual cross-section from the mean. The concentration of each element was the highest possible, but, with the exception of tungsten, this was small in the case of powders.

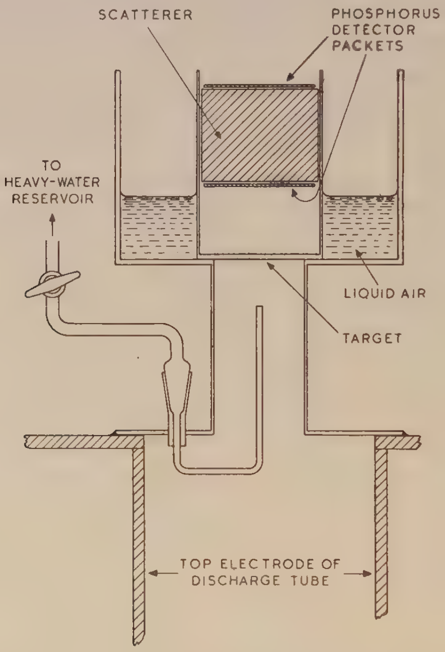

Figure 1. Arrangement for producing the heavy-ice target and geometry of the scatterer and detectors.

Since the geometry used in the present scattering experiments was not ideal, only relative cross-sections could be measured. The standard cross-section for reference purposes is usually taken to be that of paraffin wax; taking the consensus of most observations, the total scattering cross-section of hydrogen for neutrons of energy 3·25 Mev. should be about 2×10^{-24} cm.^{2} The value of $1{\cdot}8 \times 10^{-24}$ cm.^{2}

was obtained by Booth and Hurst⁽⁶⁾, using as detector an indium foil sensitive to slow neutrons. The neutrons on which these latter observations were made were of the same energy as those used in the present experiments and the geometry was good. The value given by the present experiments for the hydrogen cross-section is $1{\cdot}73 \times 10^{-24}$ cm², and is subject to two corrections. The effect of the bad geometry is to reduce the apparent cross-section by a factor of not more than 5 per cent. The second correction arises from the fact that probably one-third of the neutrons colliding with protons will be scattered forward with energy sufficient to activate the phosphorus. Not all these will pass through the second phosphorus packet, but the effect of this quasi-elastic scattering will be to reduce the apparent absorption by about 25 per cent. Hence the actual cross-section is about 25 per cent greater than the apparent on account of this forward scattering. Thus, the value of $1{\cdot}73 \times 10^{-24}$ cm² given is probably about 20 per cent too low, so that the actual value of the total proton cross-section for D–D neutrons from our experiments may be said to be in good agreement with the results of other investigators. At all events, the agreement is sufficiently good to allow our relative values to stand as absolute values without need of major correction.

Table 1

Element and atomic number	Substance used	Cross-section in 10^{-24} cm²	Estimated maximum error (per cent)
1 H	Paraffin wax	1·73	10
6 C	Carbon, vacuum purified	1·27	10
8 O	PbO_2	0·65	50
11 Na	NaCl	2·65	25
12 Mg	Mg	1·63	20
13 Al	Al	1·47	5
14 Si	CSi	1·37	16
15 P	P	1·32	15
16 S	S	1·41	10
17 Cl	CCl_4	1·45	15
19 K	KCl	2·45	25
24 Cr	Cr	1·48	9
25 Mn	Mn	1·79	12
26 Fe	Fe	1·76	8
27 Co	Co	1·76	5
28 Ni	Ni	1·62	5
29 Cu	Cu	2·02	2
30 Zn	Zn	2·28	5
48 Cd	Cd	2·46	6
53 I	I	3·7	15
	CHI_3	3·8	—
74 W	W	3·7	7
80 Hg	Hg	3·5	4
82 Pb	Pb	2·9	8
92 U	U_3O_8	5·0	40

A graph, figure 2, is given in which our results and those of Kikuchi and Aoki⁽³⁾ are exhibited on the same scale. It is seen that there is a close parallel between the curves connecting cross-section (σ) with atomic number (Z). The results of Zinn, Seely and Cohen(4) show no such parallel. This is rather surprising since the neutrons used had an energy of 3·25 Mev. in our experiments, an energy of 2·46 Mev. in the experiments of Kikuchi and Aoki, and an energy of 2·88 Mev. in the experiments of Zinn, Seely and Cohen. The latter investigators, as well as Aoki(7), have shown that, while the absorption + total scattering cross-sections of some elements are roughly independent of the incident neutron energy, the cross-sections of others may vary by as much as 40 per cent for a variation of neutron energy from 2·4 to 2·9 Mev. It is thus rather remarkable that our results should corroborate the results of Kikuchi and Aoki, rather than those of Zinn, Seely and Cohen.

It is relevant to comment that one may hardly hope to look for a fine-structure effect when the average error involved in the readings is about 10 per cent. Against this it may be noted that in estimating the error the maximum probable has always been taken, so that the actual error may well be much less. Again, while lack of time prevented a full programme of check experiments being carried out, the cross-section of iodine was measured twice; in the one set of experiments iodine itself was used as scattering material, in the other set iodoform was so used. The agreement of the results in the two cases ($3{\cdot}7$ and $3{\cdot}8\times10^{-24}$ cm^2 respectively) was well within the estimated maximum experimental error of 15 per cent.

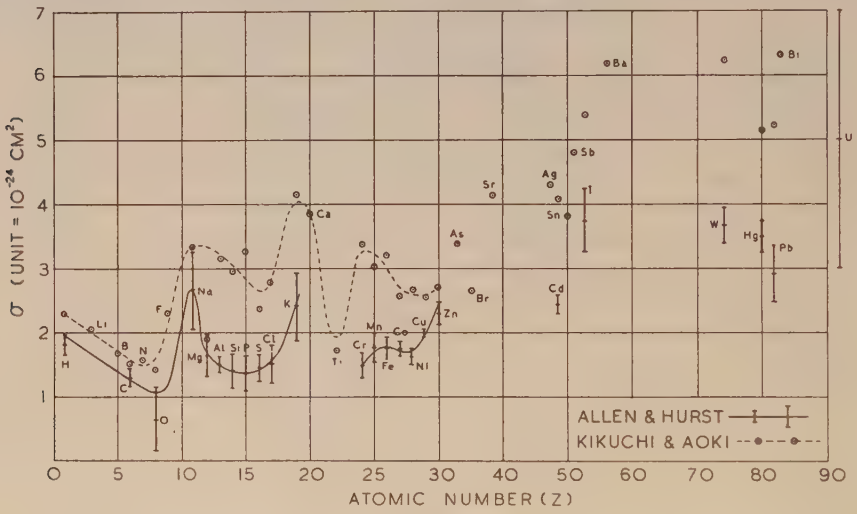

Figure 2.

It is striking that our results, in common with those of other investigators who have used as detectors elements such as iron, copper, etc., are on the average about half the values given by the observers who have used ionization chambers as detectors. It is difficult to account for this fact. For reasons already given it cannot be due to elastic scattering: this effect cannot be observed to any appreciable extent with neutrons of energy 3·25 Mev., and in any case the effect

Table 2

The cross-sections in 10^{-24} cm^2 of elements for fast neutrons as determined by various investigators

Element	Kikuchi and Aoki (D–D)	Zinn, Seely and Cohen (D–D)	Allen and Hurst (D–D)	Ladenburg and Kanner (D–D)	Dunning (Rn–Be)	Grahame and Seaborg (Rn–Be)
1 H	2·28	2·4	1·73	2·11	1·6	
1 D	1·98	2·17				
3 Li	2·01				1·6	
5 B	1·65	1·98				
6 C	1·5	1·97	1·27	1·57	1·7	0·4
7 N	1·56	1·38		1·27	1·8	
8 O	1·41	1·25	0·65	0·75		
9 F	2·3					
11 Na	3·33	2·37	2·65			
12 Mg	1·89	2·25	1·63			
13 Al	3·15	2·34	1·47	2·16	2·4	0·9
14 Si	2·95	2·77	1·37			
15 P	3·24		1·32			
16 S	2·38	3·12	1·41		2·7	
17 Cl	2·78	1·42	1·45			
19 K	4·15	3·13	2·45			
20 Ca	3·85					
22 Ti	1·73					
24 Cr	3·38		1·48			
25 Mn	3·02	3·82	1·79			
26 Fe	3·20	3·15	1·76		3·0	
27 Co	2·59		1·76			
28 Ni	2·66		1·62			
29 Cu	2·59	2·82	2·02		3·2	
30 Zn	2·68	3·28	2·28		3·3	1·5
33 As	3·39					
34 Se		4·05				
35 Br	2·69					
38 Sr	4·14					
42 Mo		4·06				
47 Ag	4·30					
48 Cd	4·07		2·46			
50 Sn	3·82	4·39			4·3	1·7
51 Sb	4·81					1·8
53 I	5·40		3·7		4·6	
56 Ba	6·19					
74 W	6·21		3·7		5·3	
80 Hg	5·13	5·35	3·5		5·8	
82 Pb	5·25	6·74	2·9		5·7	2·0
83 Bi	6·30					2·1
92 U			5·0			

Note.—In this table the results of Allen and Hurst and of Grahame and Seaborg are for absorption + inelastic scattering ; the remainder are total collision cross-sections.

of elastic scattering for the average element could not be much greater than it is in paraffin wax, for which material the mean free path is roughly the same as that determined by Booth and Hurst.

Of the individual values of the cross-sections, the most noteworthy is that of oxygen, which is easily the lowest observed. This is corroborated by all other investigators. Our value is close to that given by Ladenburg and Kanner (13), whose figures are all about 25 per cent higher than the corresponding figures obtained by us. Unfortunately they investigated relatively few elements, so that an extensive comparison cannot be made; but their observation of the cross-section of oxygen has the advantage that it is the only one which has so far been made on liquid oxygen, i.e. on a maximum concentration of oxygen molecules. It is interesting to note that all observers using a D–D source have found a rapid decrease in cross-section between hydrogen and oxygen.

The value of the total cross-section of iodine was found by Kikuchi and Aoki to be considerably greater than those of most of the surrounding elements, and was in fact slightly higher than the values for mercury and lead. This also is corroborated in our results. Unfortunately, Zinn, Seely and Cohen do not give a value for the scattering cross-section of iodine.

A comparative table of most of the observations of the scattering cross-sections of elements for D–D neutrons is appended.

§ 6. ACKNOWLEDGEMENTS

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THE RESOLVING POWER OF THE MAGNETIC ELECTRON LENS USED AS A BETA-RAY SPECTROMETER

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ABSTRACT. Expressions are obtained for the resolving power of the magnetic electron lens as determined by the geometry of the experimental arrangement in which it is used as a beta-ray spectrometer. This calculated distribution is then compared with the focussed spread of electron velocities observed in practice, a cloud chamber being used as recording device. The fact emerges that the influence of spherical aberration in the lens is small for the apertures here employed. The results indicate how a high resolving power may be attained in this method.

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§1. INTRODUCTION

A beta-ray spectrometer based on the selective focussing action of a magnetic lens on electrons of heterogeneous velocity was first described by Klemperer(1), and other authors have improved it(2), (3). So far, however, no attempt has been made to evaluate the theoretical resolving power of such a system and compare it with observations on the velocity spread focussed into a recording device such as a GM-counter or cloud chamber. It therefore seems useful to put forward the present simplified treatment and its experimental substantiation. The analogous problem does not arise in optics, since the dispersive power of a simple lens is not exploited in a corresponding manner.

§2. THEORETICAL

The total resolving power of any experimental arrangement will be determined by the aberrations of the electron lens as well as by the simple geometry of the beta-source, recording chamber and focussing system. In the spectrometers so far described, however, the recording aperture is so large compared with the lens aperture that the aberrations in the latter are negligible in relation to the "geometrical" resolving power as determined by the former. In the present work this latter quantity is evaluated and shown to account for nearly the whole of the observed focussing spread.

The relation between the focal-length (f) of a magnetic electron lens, the field (H_x) measured along the axis of the lens, and the velocity of the focussed electrons is most simply expressed as

$$f=4(H'\rho)^2 \Big/ \int_{-\infty}^{\infty} H_x{}^2\,dx \qquad \ldots\ldots(1),$$

where the electron is characterized by its momentum expressed in terms of the observed radius of curvature ρ of its path in a uniform transverse (Helmholtz) field, H'. In this way the need to introduce explicitly the relativistic mass correction is avoided, this being contained in the experimental quantity ($H'\rho$).

From this expression we have immediately

$$\frac{df}{d(H'\rho)}=\frac{8(H'\rho)_0}{\int_{-\infty}^{\infty} H_x{}^2\,dx}=\frac{2f_0}{(H'\rho)_0} \qquad \ldots\ldots(2),$$

where $(H'\rho)_0$ is the momentum of electrons focussed at the focal-length f_0 in the centre of the recording aperture. We may then write for the observed spread of electron momenta, $\Delta(H'\rho)$, as a fraction of the mean,

$$\frac{\Delta(H'\rho)}{(H'\rho)_0}=\frac{\Delta f}{2f_0} \qquad \ldots\ldots(3).$$

Now the range of focal-lengths embraced in the recording system is determined, apart from aberrations in the lens, directly by the geometry of the apparatus, as will be evident from a consideration of figure 1, which shows the limiting electron paths. Electrons from the source S are focussed by the field of the lens-coil LL into the window of the recording system, W; D is a central stop preventing direct radiation from reaching the window, and T is the evacuated lens-tube. The maximum and minimum electron velocities recorded with a given lens-field will clearly correspond to the maximum and minimum focal-lengths of the system, and these in turn to the greatest and least object-image distances respectively, as for a converging lens in optics. These limiting distances are realized for electron paths lying as close to the axis as the stop D allows, and suffering minimum and maximum deflection respectively in the lens-field.

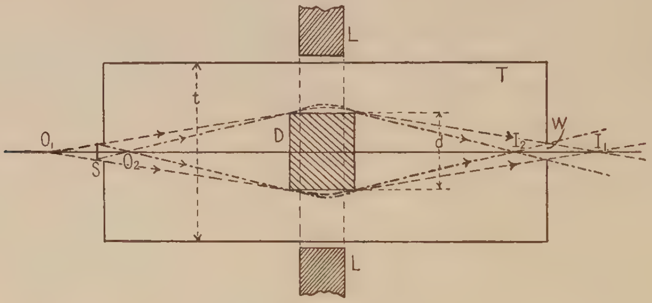

Figure 1. Limiting electron paths in lens. (Not to scale.)

Thus the greatest effective focal-length is represented by an electron path starting from the extremity of the source and just clearing D, as if projected from the point O_1 on the axis, and being then so bent in the lens that it just passes the window W to cross the axis at I_1; any path lying further from the axis will only pass the window in such a direction as to cut the axis nearer to it than I_1. Similarly, the least effective focal-length corresponds to a path from the limit of the source cutting the axis in front of it at O_2, just clearing the stop D, and lying just within the window after crossing the axis at I_2.

Simple geometrical reasoning then gives the dependence of these limits on the dimensions of the focussing system. If the source and window have extension at right angles to the axis of s and w respectively and the diameter of the stop D is d, then

$$\frac{q_1-q_0}{q_1}=\frac{w}{d}=\frac{q_0-q_2}{q_2},$$

where q_1 and q_2 are the maximum and minimum image distances respectively, and q_0 is the ("mean") image distance for electrons focussed at the centre of the window. Then

$$q_1=\frac{q_0 d}{d-w} \quad \text{and} \quad q_2=\frac{q_0 d}{d+w},$$

so that we may express the limits of the image distance as

$$q'=\frac{q_0 d}{d\pm w}.$$

In the same way it follows that the limits of the effective object distance are

$$p'=\frac{p_0 d}{d\pm s},$$

where p_0 corresponds to an incident path starting from the centre of the source and just grazing the edge of the central stop. The maximum and minimum effective focal-lengths will then occur for paths having maximum and minimum object-image distance respectively, so that these focal limits f' can be written

$$\frac{1}{f'}=\frac{1}{p'}+\frac{1}{q'}=\frac{d\pm s}{p_0 d}+\frac{d\pm w}{q_0 d}=\frac{1}{f_0}\pm\frac{1}{d}\left\{\frac{s}{p_0}+\frac{w}{q_0}\right\},$$

whence

$$\frac{1}{d}\left\{\frac{s}{p_0}+\frac{w}{q_0}\right\}=\frac{f_0-f'}{f'f_0}=\frac{\pm\Delta f}{f_0^2}$$

so long as Δf is small compared with f_0; then

$$\frac{\Delta f}{f_0}=\pm\frac{f_0}{d}\left\{\frac{s}{p_0}+\frac{w}{q_0}\right\}=\pm\frac{2\Delta(H'\rho)}{(H'\rho)_0} \qquad \text{......(4)},$$

from relation (3). This expression simplifies to

$$\frac{\Delta(H'\rho)}{(H'\rho)_0}=\pm\frac{s+w}{4d} \qquad \text{......(5)}$$

in the experimentally important case of unit magnification, when $p_0 = q_0 = 2f_0$. This gives the velocity limits of the electron band recorded within the window W, under the assumption of rectilinear paths up to and beyond the central stop. But between these limits there will be wide variation in the proportion of electrons, incident on the lens aperture, that are focussed into the recording system. For intermediate velocities, paths further from the axis than the limiting ones considered above will also bring electrons into the window. Such a path, corresponding to an increase or decrease of the effective object distance within the limits $O_1 - O_2$ (figure 1), will only pass through the window when it gives a corresponding increase or decrease in the image distance within the limits $I_1 - I_2$. That is, the focal-length of the system for such a path must lie within the above limits and, since the lens-field is assumed constant and uniform (a "perfect" lens), it follows from equation (1) that it can only be travelled by electrons of velocities lying within the limits of expression (5). For a certain narrow velocity band all electrons entering the lens aperture will follow paths passing through the window W. It is obvious that the limits of this "totally-recorded" band will be determined by the internal diameter of the lens-tube T, and it can be shown by simple geometry that it is given by

$$\frac{\Delta(H'\rho)'}{(H'\rho)_0} = \pm \frac{s+w}{4t} \qquad \ldots\ldots(6).$$

Within this velocity range, all electrons entering the annular aperture of the lens will be focussed through the window W; outside it, the proportion of incident

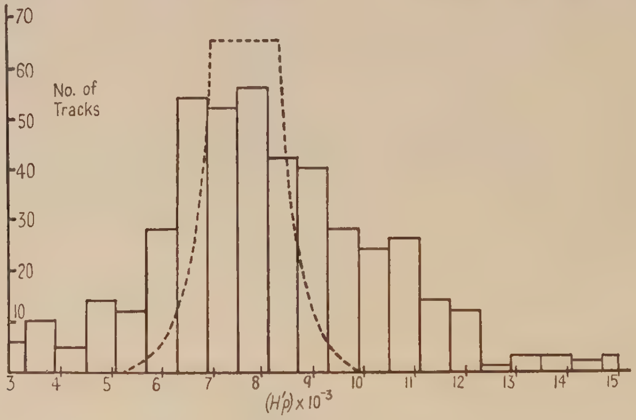

Figure 2. Momentum distribution in focussed electron band.

Calculated - - - -

Observed ⊓

electrons thus focussed will decrease until it reaches zero at the limits set by (5). This proportion varies as the square of the distance from the axis, which in turn is inversely proportional to the corresponding focussed spread, $\Delta(H'\rho)$, as (5) and (6) show. Hence the focussed fraction declines in both directions from the limits given by (6), in inverse proportion to the square of the focussed spread, as measured from the focussed mean, $(H'\rho)$. This theoretical distribution is represented by the broken line in figure 2.

§ 3. EXPERIMENTAL

The above considerations were put to the test with a large magnetic electron-lens that has been described elsewhere$^{(3)}$. It was so arranged that beta-rays were focussed through the window W into a counter-controlled cloud chamber, where their tracks were photographed. By re-projection, the radius of such tracks (ρ) in the uniform Helmholtz field (H') maintained across the chamber was determined with an accuracy of a few per cent. In this way the momenta $(H'\rho)$ of 436 electrons were found, and the frequency distribution is shown in the histogram of figure 2. The broken line gives the calculated velocity spread from expressions (5) and (6) above, the experimental dimensions being : $d=2$ cm., $t=4{\cdot}6$ cm., $s=6$ mm., $w=10\times 20$ mm. A window of this large size was used in order to get a suitable frequency of tracks; hence the wide band of velocities focussed. For purposes of comparison, the area beneath the broken line in figure 2 has been made equivalent to the total number of tracks recorded between the outer theoretical limits. The experimental value of $(H'\rho)_0$ corresponds to an accelerating potential of 1·8 Mev.

In general the agreement of the results with calculation is satisfactory. Taking into account the small "background" evident at higher and lower velocities, the agreement is very good on the low-energy side of the mean. In the other direction, however, there is a large excess of electrons above the expected upper focussing limit, much bigger than possible experimental error. It is probable that this arises mainly from scattering from the internal lead shielding between the source and lens ; beyond the lens, the shielding is so disposed that scattering into the beam is only possible by two or more successive reflections, and hence only occurs with small probability. Before the lens, however, small-angle scattering from the horizontal surfaces of the lead can bring high-energy electrons into the lens-field at such an angle that the small deviation suffered will now carry them into the aperture of the window, whereas unscattered electrons of the same velocity can only enter the lens at angles resulting in deviations insufficient to bring them within W. In the case of electrons scattered into the lens parallel to the axis the effective focal-length of the system is doubled, if object and image distances are equal, as in normal practice. From equation (1) it follows that electrons of momentum up to 40 per cent greater than the mean could in such circumstances be focussed into the centre of the final window; allowing for the breadth of the latter, a decreasing proportion of faster electrons up to a limit of almost 70 per cent above the mean could be recorded. It will be seen that this is roughly the extent of the high-energy spread observed (figure 2). If this explanation is correct, the amount of scattering occurring is considerable; it could be reduced by lining the lead shielding with aluminium or wax. A similar effect beyond the low-energy limit is not to be expected: slower electrons will only be focussed into the final window if they enter the lens-field at a much greater angle to the axis than is made by the direct path, and there is a rapid decrease in the amount of scattering with angle.

A contribution to the high-energy excess might also arise from spherical aberration in the lens, but can only be small with such apertures as here used ($f/10$, in the optical sense). The extreme limits of focussing are determined by the conditions at the boundaries of the central stop D and, as the considerations at the end of the last section show, spherical aberration can only extend these limits if the radial field increases in direct proportion to the distance from the axis. Such a rapid variation of the field does not exist in the present experimental conditions(3). The most that spherical aberration can effect is a rounding-off of the distribution peak (figure 2), particularly on the low-energy side, and a general rise in the proportion of focussed electrons on the high-energy side, resulting in a displacement in this direction of the peak as a whole. Thus the effect is in the same direction as that experimentally observed, but in radial fields of the values here employed it can only be of the order of a few per cent of the mean. Hence the major rôle must be ascribed to the scattering effect discussed above.

Davies and O'Ceallaigh(2) pointed out that the Helmholtz field of the cloud chamber might have an important influence on the spread of electrons focussed, filtering out from the beam the more readily deflected slower components. This possibility was investigated by mapping the Helmholtz field here employed and then making point-to-point plots of the electron paths. The apparatus was set up so that the paths of electrons of "mean" focussed velocity passed through the centre of the window of the cloud chamber. The focussing limits were determined by a preceding window, and between this and the latter there were no restrictions on the electron beam width. As a result the Helmholtz field could only remove a small proportion of the slowest electrons from the beam, without any compensatory increase occurring on the high-energy side; hence it can play no significant part in producing the observed distribution.

§4. CONCLUSION

The expressions deduced for the simple resolving power of a magnetic focussing system account largely for the experimentally observed velocity spread of focussed electrons. The effect of spherical aberration is small with the type of field and the apertures here used, and the disturbing effect of the Helmholtz field is negligible. The observed excess of focussed electrons of high velocity is to be ascribed to selective scattering from the internal shielding of the system, and should be amenable to reduction. The main requirements for more accurate use of the lens as a beta-ray spectrometer follow directly from these results. The geometrical resolving power [cf. equations (5) and (6)] can be improved considerably by reduction in diameter of the window and source, and by the use of a narrow annular lens-field; by these measures it should be capable of reduction to below 1 per cent.

ACKNOWLEDGEMENTS

The author is indebted to Prof. P. M. S. Blackett for his constant interest and encouragement, and to the Government Grant Committee of the Royal Society for an apparatus grant.

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THE APPLICATION OF IONOSPHERIC DATA TO RADIO-COMMUNICATION PROBLEMS: PART I

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ABSTRACT. The reflection of waves obliquely incident on the ionosphere is studied theoretically. A direct method of calculating the maximum usable frequency reflected at oblique incidence by a thick " parabolic " layer, for both short-distance (plane earth) and long-distance (curved earth) transmission, is developed, and the results exhibited graphically. In an appendix it is shown how the thickness of a " parabolic " layer may be deduced from the results of vertical-incidence ionospheric sounding.

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§ 1. INTRODUCTION

In this paper we consider methods whereby ionospheric data obtained from vertical-incidence measurements can be employed in attempting to assess the relative usefulness of different frequencies for long-distance communication, assuming that such communication is effected by waves refracted by the ionosphere. For reasons which will emerge in the course of the discussion we shall be concerned principally with problems of short-wave transmission.

It is convenient first to recapitulate that the ionosphere may be regarded as composed of two main layers, the upper of which shows a dual structure when the sun's zenith distance is small. Both of these layers are sufficiently ionized to refract short waves, and so must be considered as bending agencies. The radio engineer is, however, interested not only in the question whether waves are deviated back to the ground or not, but also in the absorption suffered by the waves in their journey to the deviating layer and back. In this paper we are therefore concerned primarily with estimating the range of frequencies which are deviated by the ionosphere at oblique incidence and therefore suitable for practical communication over various distances. In a later paper the attenuation of such refracted waves in their passage through the ionosphere will be discussed quantitatively.

§ 2. ABSORPTION- AND ELECTRON-LIMITATION

In an early communication on long-distance short-wave transmissions (1) it was pointed out that there were two factors which had to be considered when the suitability of any particular frequency for communication over a fixed distance was under discussion. The frequency must be sufficiently low for propagation not to be electron-limited, that is to say the waves must not escape from the ionosphere by penetration. Secondly, the absorption must be as low as possible. In the latter connexion it is clear that if the major absorption occurs in the transit through the lower ionosphere, and if, as other evidence suggests, we can assume that $\nu^2 \ll p^2$ for short waves, where ν is the collisional frequency and p is the angular frequency of the waves, the attenuation can theoretically be expressed as $e^{-\gamma}$, where γ is approximately inversely proportional to p^2. Appleton has shown[(2)] that the experimental results of Burrows[(3)] for transatlantic communication are in agreement with such a law. We may illustrate this, using Burrows' results, in the following way. Let S be the received signal strength in microvolts per metre per kilowatt radiated. Then $-\log_e S$ is proportional to the attenuation factor γ. The relation between $-\log_e S$ and f, the frequency, is plotted in figure 1. This figure shows that the absorption is first reduced as the frequency is increased, but as electron-limitation becomes progressively operative for the multiply-reflected rays, the signal level is gradually reduced until ultimately there is not even the singly-reflected ray, and refracted rays entirely disappear.

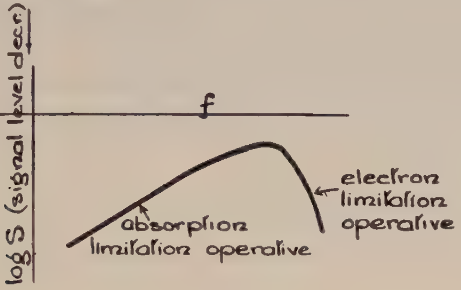

Figure 1.

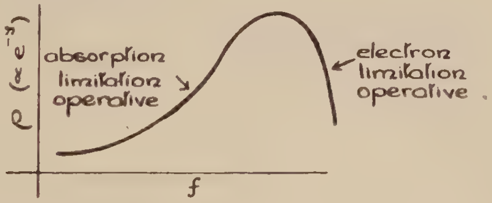

Figure 2.

If we regard matters from a slightly different standpoint and think of the ionosphere as possessing a reflection coefficient ρ we can illustrate the relation between ρ and f as shown in figure 2. Here the ordinates plotted are proportional to $e^{-\gamma}$, which quantity is proportional to ρ. From such considerations it is clear that, to obtain maximum signal strength, the frequency employed should be as high as possible compatible with the effects of electron-limitation being inappreciable.

§ 3. THE (P, f) RELATIONS FOR NORMAL AND OBLIQUE INCIDENCE

The behaviour of the ionosphere in reflecting waves of different frequencies is usually interpreted in terms of the relation between the equivalent or group path P' and frequency f. It is usual to determine this relation experimentally for the case of vertical incidence, under which condition the equivalent path P' is equal to twice the equivalent height h'. We now briefly consider two methods, (*a*) and (*b*) immediately below, whereby the (P', f) relation for oblique incidence can be deduced from the vertical incidence (P', f) data [(4),(5),(6) (7)]. We shall, throughout our discussion, neglect the influence of the earth's magnetic field, so that our deductions will apply approximately to the case of ordinary-ray propagation.

(*a*) Suppose the ordinary-ray (P', f) curve for vertical incidence is as shown in figure 3. Let D be the fixed distance of transmission. We can find the (P', f) curve for oblique transmission over a plane earth in the following way.

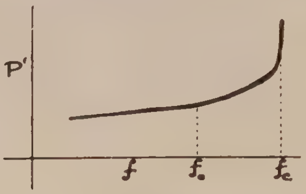

Figure 3.

Consider the frequency f_0 which corresponds to $P'_{(f_0, 0)}$, and let

$$D = \tan i_0 \,.\, P'_{(f_0, 0)} \qquad \ldots\ldots(1).$$

Then the angle i_0 is the angle of incidence which a certain new frequency f must have in order that it shall arrive back at the ground at a distance D.

Also we have

$$f = f_0 \sec i_0 \qquad \ldots\ldots(2)$$

and

$$P'_{(f_0 \sec i_0,\, i_0)} = D \operatorname{cosec} i_0 \qquad \ldots\ldots(3).$$

From these three equations we can find the new (P', f) curve for any given distance D. For any frequency f_0 we determine i_0 from equation (1). The corresponding frequency and equivalent path for the oblique case are then given in equations (2) and (3) respectively.

(*b*) The oblique-incidence curve can also be deduced from the normal-incidence curve by using Martyn's theorem in the following manner.

From this theorem we know that

$$P'_{(f_0, i)} = \sec i \; P'_{(f_0 \cos i,\, 0)}.$$

Thus if we know the value of i we can find the value of $P'_{(f_0, i)}$ appropriate for transmission of frequency f_0 over distance D, where $D = \sin i \,.\, P'_{(f_0, i)}$.

From the last two equations we have

$$D \cot i = P'_{(f_0 \cos i,\, 0)} \qquad \ldots\ldots(4).$$

We therefore plot a curve showing the relation between $D \cot i$ and $f_0 \cos i$ and lay this on the vertical-incidence (P', f) curve as shown in figure 4. The two points of intersection give the two appropriate values of i for the two rays. When these are found, say i_1 and i_2, we can calculate from Martyn's theorem the relevant values of P'.

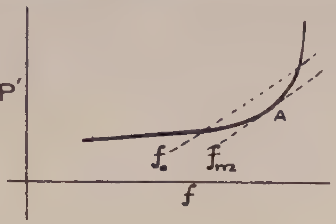

Figure 4.

Having drawn a curve for a frequency f_0 it is easy to estimate graphically to what value f_0 must be increased in order that the curve shall touch the vertical-incidence (P', f) curve at a single point A. In this way the maximum usable frequency can be deduced.

§ 4. THE TRAJECTORIES OF WAVES OBLIQUELY INCIDENT ON THE IONOSPHERE

It is convenient to consider first the case of a relatively thin layer such as the abnormal E-region. Under these conditions we merely want to know the height of the layer h_0 and the critical penetration frequency at vertical incidence f_c, to enable us to predict the behaviour of the layer to obliquely incident rays. We consider first the case of propagation over distances sufficiently small for the earth's surface to be considered plane. Subsequently we deal with the case of longer distances of transmission in which the curvature of the earth must be considered.

(a) *Case of thin layer and flat earth*

In this case let μ be the refractive index within the layer at the level where the ray is reflected. Referring to figure 5, we have

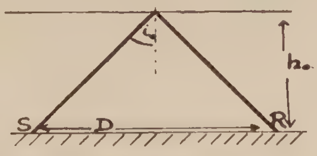

Figure 5.

$$\mu^2 = \sin^2 i_0 = 1 - f_0{}^2/f^2,$$

where f is the frequency used.* Now $\tan i_0 = D/2h_0$ and therefore

$$f_0{}^2 f^2 = 4h_0{}^2/(4h_0{}^2 + D^2).$$

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* The frequency f_0 is that for which the refractive index of the medium at the top of the trajectory within the layer becomes zero.

This result may be expressed in two ways. If f refers to the maximum usable frequency at distance D we have

$$f_{\max} = f_c \sqrt{[(4h_0^2 + D^2)/4h_0^2]} \qquad \ldots\ldots(5).$$

If on the other hand we wish to state the skipped distance for a certain frequency we have

$$D_{\text{skip}} = 2h_0 \sqrt{\left(\frac{f^2}{f_c^2} - 1\right)} \qquad \ldots\ldots(6).$$

(b) *Case of thin layer and curved earth*

This case has been dealt with by Appleton (1) in his discussion of electron limitation. Referring to figure 6 we have

$$D = 2R\theta$$

and

$$\cos^2 i_0 = \frac{(h_0 + R - R\cos\theta)^2}{(h_0 + R - R\cos\theta)^2 + R^2\sin^2\theta}.$$

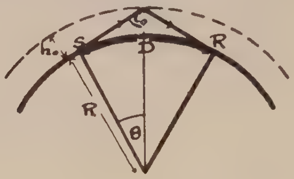

Figure 6.

Now since θ in all cases is small, this becomes

$$\cos^2 i_0 = \frac{f_0^2}{f^2} = \frac{(h_0 + \frac{1}{2}R\theta^2)^2}{(h_0 + \frac{1}{2}R\theta^2)^2 + R^2\theta^2}.$$

Substituting now for D we have

$$\frac{f_0^2}{f^2} = \frac{(h_0 + D^2/8R)^2}{(h_0 + D^2/8R)^2 + D^2/4}.$$

If f now refers to the maximum usable frequency for distance D we have

$$f_{\max} = f_c \sqrt{\left[\frac{4(h_0 + D^2/8R)^2 + D^2}{4(h_0 + D^2/8R)^2}\right]} \qquad \ldots\ldots(7).$$

(It will be seen that when $R = \infty$ this formula reduces to the plane-earth formula given above.) The relation (7) is illustrated for two practical cases of $h_0 = 110$ and 300 km. respectively in figure 7, where $f_{\max}/fc$ is plotted as a function of D.

It is now of practical interest to pursue the calculation a little further and to find directly the maximum usable frequency for round-the-world transmission. Due to the curvature of the earth there is a maximum value of D, which is given by

$$D^2_{\max} = 8Rh_0.$$

Substituting in (7), we have in this case

$$f_{\max} = f_c\sqrt{(1 + R/2h_0)} \simeq f_c\sqrt{(R/2h_0)} \qquad \ldots\ldots(8).$$

This is an important practical formula, and from it we learn that in the case of the abnormal E-layer with $h_0 = 110$ km. we have $f_{\max} = 5{\cdot}4 f_c$. In the case of the F layer, where we can take $h_0 = 300$ km., we have $f_{\max} = 3{\cdot}26 f_c$, or if $h = 250$ km., $f_{\max} = 3{\cdot}58 f_c$. (Actually the factor 3·5 is found to be a useful practical figure.)

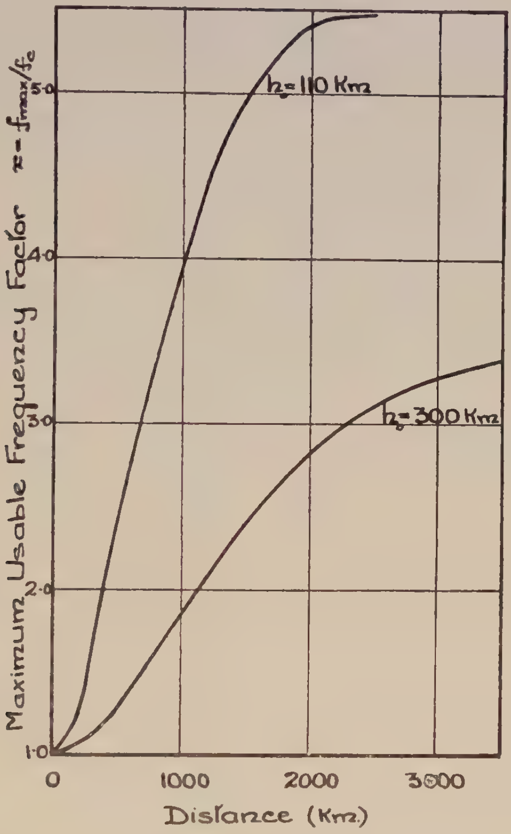

Figure 7. Typical curves calculated from formula (7).

We now consider the changes necessary in the case of the above if the refracting layer can no longer be considered thin. In such a case we can use the parabolic-layer treatment previously developed$^{(2)}$. Throughout this discussion we assume that there is no horizontal ionization-gradient in the layer. We consider the case of a flat earth first.

(c) *Case of thick layer and flat earth*

Consider a parabolic layer of semi-thickness y_m the lower boundary of which is situated at a height h_0 above the ground. Let f_c be the critical penetration frequency of the layer at vertical incidence. The equivalent path P' of the ray travelling as shown in figure 8 over a fixed distance of transmission D is then given by

$$P' = y_m \frac{f}{f_c} \log_e \left(\frac{f_c + f \cos i_0}{f_c - f \cos i_0} \right) + \frac{2h_0}{\cos i_0}. \qquad \ldots\ldots(9).$$

The first term on the right-hand side represents the equivalent path within the layer itself, while the second term expresses the path in the un-ionized stratum between the layer and the ground. f_c is the critical frequency at vertical incidence.

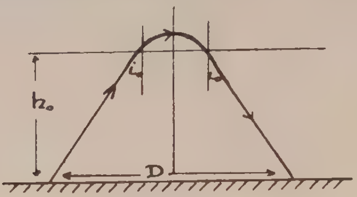

Figure 8.

Relating P' to D, the distance of transmission, we have also

$$D = P' \sin i_0 \qquad \ldots\ldots(10),$$

so that

$$D = y_m \frac{f}{f_c} \sin i_0 \log_e \left[\frac{1 + \frac{f}{f_c} \cos i_0}{1 - \frac{f}{f_c} \cos i_0} \right] + 2h_0 \tan i_0 \qquad \ldots\ldots(11).$$

Now in dealing with the two formulae immediately above we can proceed in two ways:—

(a) Find P' as a function of f for different fixed values of D

or (b) Find D as a function of i_0 for different fixed values of f.

In case (a), we find that the relation between P' and f is as shown in figure 9, showing that, for a certain range of frequencies, there are two possible paths. The maximum frequency usable in such a case is shown as f_m.

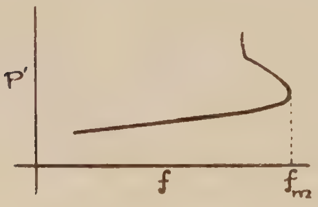

Figure 9.

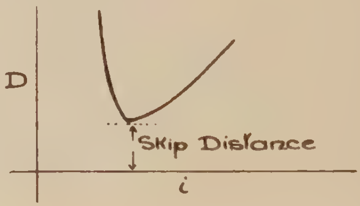

Figure 10.

In case (b) the relation between D and i_0 (for constant f) is as shown in figure 10. Here it will be seen that for distances beyond the skip-distance there are two possible angles of incidence by way of which rays may travel a constant distance.

(d) *Case of thick layer and curved earth*

Let i_0 be the angle of incidence on the layer which is situated at a height h_0 above the spherical earth (figure 11). We proceed to find the value of the part-range D_1.

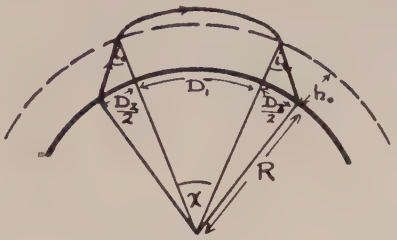

Figure 11.

Let i be the angle the ray makes with the normal at any point in the layer, distant r from the centre of the earth. Then, according to Bouger's rule we have

$$\mu r \sin i = \mu_0 r_0 \sin i_0 = (R+h_0) \sin i_0,$$

where $$r_0 = R + h_0.$$

Thus $$\tan i = \sin i/\sqrt{(1-\sin^2 i)} = r_0 \sin i_0/\sqrt{(\mu^2 r^2 - r_0{}^2 \sin^2 i_0)}.$$

Now from the diagram

$$\tan i = r\frac{d\chi}{dr} \quad \text{or} \quad d\chi = \frac{dr}{r}\tan i,$$

whence $$\chi = \int \frac{r_0 \sin i_0}{r\sqrt{(\mu^2 r^2 - r_0{}^2 \sin^2 i_0)}}\,dr.$$

Now the refractive index μ varies with the height y above the level h_0. Let us write it

$$\mu^2 = 1 - \alpha y + \beta y^2.$$

On substitution in the last integral we get a very complicated and intractable expression, but Försterling and Lassen(8) have shown that since $h_0/R \ll 1$, it can be reduced to

$$\chi = \frac{\sin i_0}{r_0}\int \frac{dy}{\sqrt{\left[\cos^2 i_0 - \left(\alpha - \frac{2}{r_0}\sin i_0\right)y + \beta y^2\right]}}.$$

$$\therefore \quad D_1 = R\chi = \frac{R \sin i_0}{r_0}\int \frac{dy}{\sqrt{\left[\cos^2 i_0 - \left(\alpha - \frac{2}{r_0}\sin^2 i_0\right)y + \beta y^2\right]}}$$

$$= \frac{R \sin i_0}{r_0}\int \frac{dy}{\sqrt{(\cos^2 i_0 - \alpha' y + \beta y^2)}},$$

where $$\alpha' = \alpha - \frac{2}{r_0}\sin^2 i_0.$$

Thus
$$D_1 = \frac{R\sin i_0}{r_0}\frac{1}{\sqrt{\beta}}\log_e\left(\frac{\alpha' + 2\sqrt{\beta}.\cos i_0}{\alpha - 2\sqrt{\beta}.\cos i_0)}\right).$$

Since
$$\mu^2 = 1 - \frac{2f_c{}^2 y}{f^2 y_m} + \frac{f_c{}^2 y^2}{f^2 y_m{}^2},$$

we have
$$\alpha = 2f_c{}^2/f^2 y_m \quad \text{and} \quad \beta = f_c{}^2/f^2 y^2{}_m.$$

$$\therefore \qquad D_1 = \sin i_0 \frac{R}{r_0}\frac{f y_m}{f_c}\log_e\left[\frac{\dfrac{2f_c{}^2}{f^2 y_m} - \dfrac{2}{r_0}\sin^2 i_0 + \dfrac{2f_c}{f y_m}\cos i_0}{\dfrac{2f_c{}^2}{f^2 y_m} - \dfrac{2}{r_0}\sin^2 i_0 - \dfrac{2f_c}{f y_m}\cos i_0}\right]$$

or
$$D_1 = \frac{R}{(R+h_0)}\sin i_0 x y_m \log_e\left[\frac{1 - x^2\dfrac{y_m}{R+h_0}\sin^2 i_0 + x\cos i_0}{1 - x^2\dfrac{y_m}{R+h_0}\sin^2 i_0 - x\cos i_0}\right] \qquad \ldots\ldots(12),$$

where $x = f/f_c$.

$$D_2 \simeq 2R\cot i_0 - 2R\sqrt{(\cot^2 i_0 - 2h_0/R)}, \qquad \ldots\ldots(13),$$

so that

$$D_1 + D_2 = \frac{R}{R+h_0}\sin i_0 x y_m \log_e\left[\frac{1 - x^2\dfrac{y_m}{R+h_0}\sin^2 i_0 + x\cos i_0}{1 - x^2\dfrac{y_m}{R+h_0}\sin^2 i_0 - x\cos i_0}\right]$$
$$+ 2R\cot i_0 - 2R\sqrt{(\cot^2 i_0 - 2h_0/R)} \qquad \ldots\ldots(14).$$

It is of interest to compare this quantity with the corresponding range in the case of a plane earth. In the latter case we had (equation 11)

$$\text{range} = \sin i_0 . x y_m \log_e\frac{1 + x\cos i_0}{1 - x\cos i_0} + 2h_0\tan i_0\ ;$$

the two expressions are very similar. In fact we can say that a curved earth behaves very much like a plane earth if we assume that the critical frequency f_c is reduced to

$$f_c - \frac{f^2 y_m}{f_c r_0}\sin^2 i_0.$$

We can now plot the relation between range (i.e. $D_1 + D_2$) and i_0 for constant f and so find when the range is a minimum. This gives the value of the maximum usable frequency for that range.

§ 5. THE DIRECT CALCULATION OF MAXIMUM USABLE FREQUENCIES

Since the maximum usable frequency is an important practical quantity it is desirable to be able to deduce it directly without having to determine the whole of the oblique (P', f) relation. We now describe a method whereby this can be achieved.

(a) *Case of plane earth*

For a plane earth and ionosphere, the expression for the distance D from sender to receiver is, as shown previously (eq. (11)),

$$D = y_m x \sin i_0 \log_e \frac{1+x\cos i_0}{1-x\cos i_0} + 2h_0 \tan i_0,$$

where i_0 = angle of incidence on the ionized layer,
y_m, h_0 are respectively the semi-thickness and height of the layer,

and $$x = \frac{\text{Frequency used } (f)}{\text{Critical frequency at vertical incidence } (f_c)}.$$

For any given frequency and layer constants the condition of maximum or minimum D will be given by $dD/di_0 = 0$. The relation between i_0 and x, for minimum D, is thus readily found to be

$$2\tan^2 i_0 \left\{ \left(\frac{x'^2}{1-x'^2} \right) \frac{y_m}{h_0} - 1 \right\} = \frac{y_m}{h_0} \,.\, x' \,.\, \log_e \frac{1+x'}{1-x'} + 2 \quad \ldots\ldots(15),$$

where $x' = x\cos i_0$.

The solution of (15) permits the direct calculation of maximum usable frequencies. In solving it the procedure adopted is to insert chosen values of x', solve for i_0, and then determine the corresponding x from the relation $x = x' \sec i_0$.

It will be noted that the relation between angle of incidence i_0 and f/f_c for minimum D (or in other words between i_0 and $f_{\max}/f_c$ for any D) depends only on the ratio y_m/h_0 and not on the absolute magnitude of either the thickness or the height of the region. (A note on a method of deducing y_m and h_0 for a " parabolic" layer is given in the Appendix to this paper.)

For any given frequencies we can thus obtain the appropriate values of i_0. Insertion of these values of i_0 in equation (11) yields the minimum distances corresponding to these frequencies, or conversely, the maximum usable frequencies for specific distances. Typical curves obtained from formulae (15) and (11) are shown in figures 12 and 13. In deriving formula (11) the effect of group retardation due to transmission through lower ionized regions has not been considered. We may, however, allow approximately for such group-retardation effects if values of the equivalent height are used in the calculations instead of values of the actual height. Further comment on this matter will be made in a later paper.

(b) *Case of curved earth*

For transmission distances up to about 500 km. the curvature of the earth can reasonably be neglected. At greater distances, however, the curvature of the earth must be considered.

To a first order of approximation a solution of the curved earth and ionosphere problem can be made on the lines of that given above for the plane earth case.

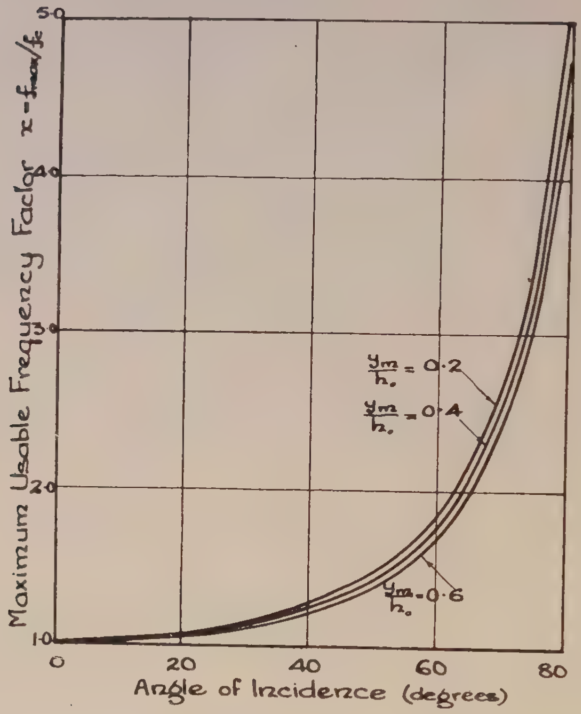

Figure 12.

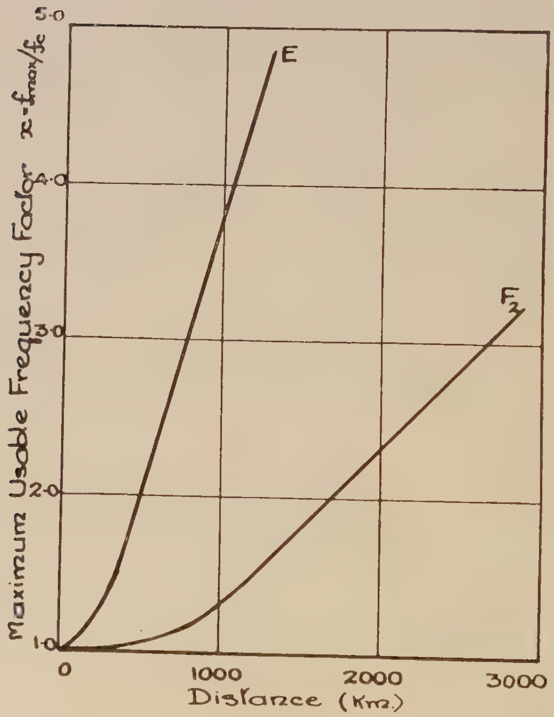

Figure 13.

Typical curves calculated from formulae (11) and (15) for regions E and F_2.

For the part-range D_1 (see figure 11) we obtained

$$D_1 = \frac{R}{(R+h_0)} \,.\, x \,.\, y_m \,.\, \sin i_0 \,.\log_e \left[\frac{1 - \dfrac{x^2 y_m}{(R+h_0)} \sin^2 i_0 + x \cos i_0}{1 - \dfrac{x^2 y_m}{(R+h_0)} \sin^2 i_0 - x \cos i_0} \right],$$

where $x = f/f_c$.

To the first order of approximation (higher order terms than those in $1/R$ being neglected), we have

$$D_1 = (1 - h_0/R) \,.\, x \,.\, y_m \sin i_0 \,.\, \log_e \left[\frac{1 + (x \cos i_0) \Big/ \left(1 - \dfrac{x^2 y_m \sin^2 i_0}{R}\right)}{1 - (x \cos i_0) \Big/ \left(1 - \dfrac{x^2 y_m \sin^2 i_0}{R}\right)} \right].$$

On expansion this can be written

$$D_1 = 2\left(1 - \frac{h_0}{R}\right) x \,.\, y_m \sin i_0 \left\{ x \cos i_0 + \frac{1}{3} x^3 \cos^3 i_0 + \ldots \right.$$

$$\left. \ldots + x \cos i_0 \frac{x^2 y_m \sin^2 i_0}{R} + x^3 \cos^3 i_0 \frac{x^2 y_m \sin^2 i_0}{R} + \ldots \right\}$$

or

$$D_1 = \left(1 - \frac{h_0}{R}\right) \,.\, x \,.\, y_m \sin i_0 \left\{ \log_e \frac{1 + x \cos i_0}{1 - x \cos i_0} + \frac{2x^3 y_m \cos i_0 \sin^2 i_0}{R(1 - x^2 \cos^2 i_0)} \right\}.$$

Differentiating with respect to i_0, we then find

$$\frac{dD_1}{di_0} = \left(1 - \frac{h_0}{R}\right) y_m x' \left\{ \log_e \frac{1 + x'}{1 - x'} + \frac{2x'^3 y_m \tan^2 i_0}{R(1 - x'^2)} \right\} + 2\left(1 - \frac{h_0}{R}\right) \frac{y x'^2 \tan^2 i_0}{1 - x'^2}$$

$$\times \left\{ \frac{2x'^2 y_m}{R} - 1 - \frac{y_m}{R} x'^2 \frac{(1 + x'^2)}{(1 - x'^2)} \tan^2 i_0 \right\} \quad \ldots\ldots(16),$$

where x' is written for $x \cos i_0$.

For the part-range D_2 we had

$$D_2 = 2R \cot i_0 \left\{ 1 - \sqrt{\left(1 - \frac{2h_0 \tan^2 i_0}{R}\right)} \right\}.$$

If only terms in $1/R$ are included, this becomes

$$D_2 = 2h_0 \tan i_0 \left\{ 1 + \frac{h_0}{2R} \tan^2 i_0 \right\},$$

whence

$$\frac{dD_2}{di_0} = 2h_0 \left\{ 1 + \tan^2 i_0 \left(1 + \frac{3h_0}{2R}\right) + \frac{3h_0}{2R} \tan^4 i_0 \right\} \quad \ldots\ldots(17).$$

The total range is given by $(D_1 + D_2)$, and for a minimum we require

$$\frac{d}{di_0}(D_1 + D_2) = 0 \,.$$

Adding expressions (16) and (17), rearranging terms and equating to zero, we find

$$\begin{aligned}\tan^4 i_0 &\left\{\frac{3h_0}{R} - \frac{2h_0}{R}(1+x'^2)\left(\frac{y_m}{h_0}\frac{x'^2}{1-x'^2}\right)^2\right\} \\ &+2\tan^2 i_0\left\{\left(3x'^2\frac{y_m}{h_0}+1\right)\frac{y_m}{R}\frac{x'^2}{(1-x'^2)}+\frac{3h_0}{2R}+1-\frac{y_m}{h_0}\frac{x'^2}{(1-x'^2)}\right\} \\ &+\frac{y_m}{h_0}x'\log_e\frac{1+x'}{1-x'}+2-\frac{y_m}{R}x'\log_e\frac{1+x'}{1-x'}=0 \qquad \text{......(18 } a\text{).}\end{aligned}$$

This expression can be written in the form

$$\begin{aligned}2\tan^2 i_0&\left\{1-\frac{y_m}{h_0}\cdot\frac{x'^2}{1-x'^2}\right\}+\frac{y_m}{h_0}.x'.\log_e\frac{1+x'}{1-x'}+2 \\ &+\frac{h_0}{R}\{A\tan^4 i_0+B\tan^2 i_0-C\}=0 \qquad \text{......(18 } b\text{),}\end{aligned}$$

where

$$A=2\left\{\frac{3}{2}-(x'^2+1)\left(\frac{y_m}{h_0}\frac{x'^2}{1-x'^2}\right)^2\right\},$$

$$B=2\left\{\frac{y_m}{h_0}\frac{x'^2}{1-x'^2}\left(3x'^2\frac{y_m}{h_0}+1\right)+\frac{3}{2}\right\}$$

and

$$C=\frac{y_m}{h_0}x'\log_e\frac{1+x'}{1-x'}.$$

The principal part of equation (18 *b*) is identical with that obtained for a plane earth and ionosphere (equation 15), the effect of the curvature of the earth being represented by the term

$$\frac{h_0}{R}\{A\tan^4 i_0+B\tan^2 i_0-C\}.$$

Accurate values of i_0 for different values of x can be obtained from equation (18 *a*), but it is found that, for the extreme practical values of h_0 and y_m/h_0, the errors introduced into the final values of (D_1+D_2) by neglecting the term in h_0/R are quite negligible for most values of i_0. Even for the limiting values of i_0 (about 73° for region F_2 and 80° for region E) the errors in (D_1+D_2) introduced by using equation (15) only amount to about $2\frac{1}{2}$ per cent. In any case, in view of the other simplifications made in the calculation (e.g. we have assumed no variation in ionosphere characteristics with latitude and longitude over the part-range D_1), the use of the more exact expression (18 *a*) in place of the simpler expression (15) is hardly justifiable. Using curves obtained from equation (15), values of (D_1+D_2), the minimum distances for curved-earth conditions, can readily be calculated.

A typical calculation is given in outline below. The procedure adopted is to select a series of values of x and to read off the corresponding values of i_0 from figure 12. D_1 is then calculated from formula (12) and D_2 is read off from a large-scale graph connecting i_0 and D_2.

Example

$$y_m = 96 \text{ km.},$$
$$h_0 = 240 \text{ km.},$$

so that
$$y_m/h_0 = 0{\cdot}4.$$

$x = \dfrac{f_{\max}}{f_c}$	i_0 (figure 12)	D_1 formula (12) (km.)	D_2 (km.)	(D_1+D_2) (km.)
1·2	37° 15′	265	370	635
1·5	53° 0′	355	670	1025
2·0	63° 52′	534	1070	1604
2·5	69° 45′	748	1560	2308
3·0	73° 15′	1283	2290	3573

A graph of x against the total range $(D_1 + D_2)$ is shown in figure 14. Knowing the vertical-incidence critical frequency f_c, the maximum usable frequency corresponding to any distance from sender to receiver can thus readily be deduced.

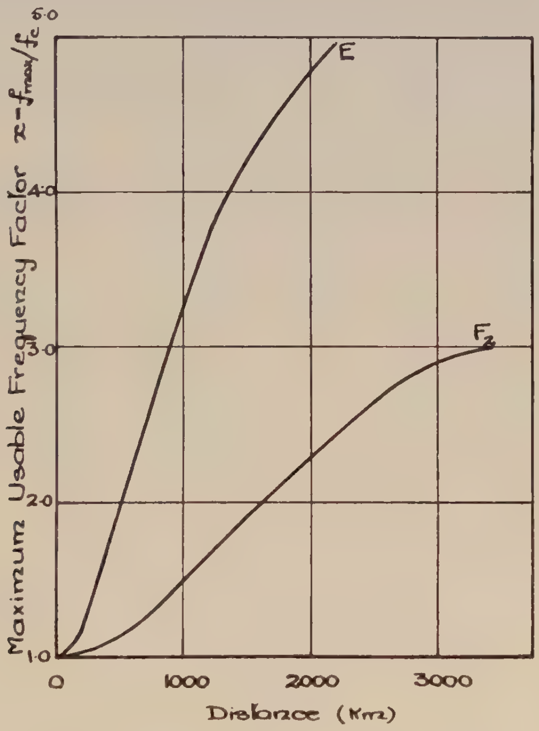

Figure 14. Typical curves for regions E and F_2.

As previously stated, our calculations of the maximum usable frequency have been directed to the case of ordinary-ray transmission, although it is known from the magneto-ionic theory (9), (10), (11) that under given conditions the reflection of the extraordinary ray persists to slightly higher values of frequency. An examination of the small correction required in practical cases has been made by Newburn Smith (12).

§ 6. SUMMARY

The reflection of waves obliquely incident on the ionosphere is studied theoretically. A direct method of calculating the maximum usable frequency reflected by a thick "parabolic" ionized layer, for both short and long distances of transmission, is developed, and the results exhibited graphically.

§ 7. ACKNOWLEDGEMENTS

The work described above was carried out as part of the programme of the Radio Research Board, and this paper is published by permission of the Department of Scientific and Industrial Research.

APPENDIX

Note on a method of deducing the thickness of a "parabolic" layer

Suppose y_m is the semi-thickness of the layer and h_0 the height of the lower boundary above the ground. Let f_c be the critical frequency of the layer at vertical incidence. The relation between equivalent height h' and frequency f is then

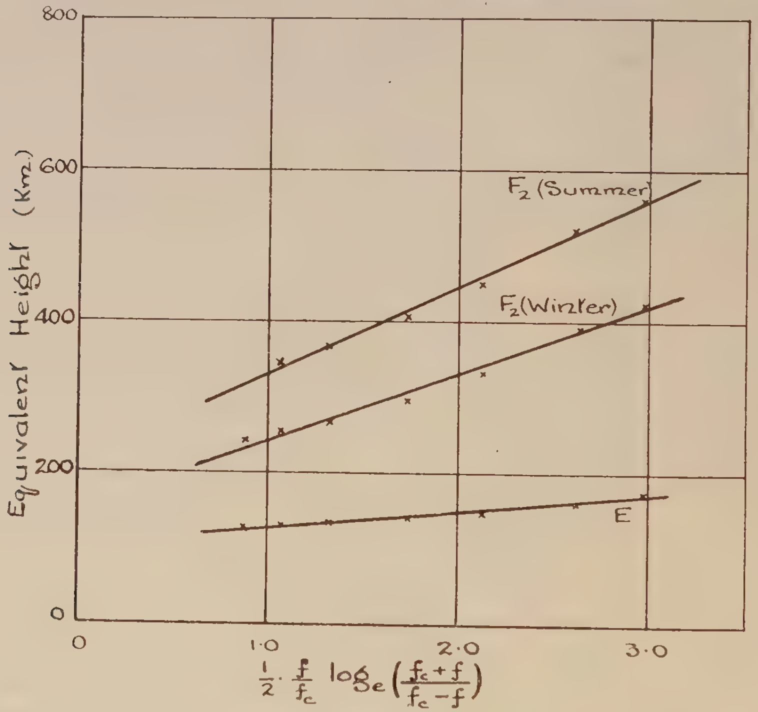

Figure 15.

$$h' = h_0 + \frac{y_m}{2}\frac{f}{f_c}\log_e\frac{f_c+f}{f_c-f}.$$

The relation between h' and $\frac{1}{2}\frac{f}{f_c}\log_e\frac{f_c+f}{f_c-f}$ is thus linear and the slope of the straight line obtained by plotting these two quantities is given by y_m. Experimental points and mean straight lines drawn from observed (h', f) data are shown in figure 15. In the case of the Region-E example the points are seen to lie very close to the straight line to be expected for a "parabolic" layer. In the case of the Region-F_2 examples there is seen to be a greater scattering of the points, which tends to reduce somewhat the accuracy of the determination of h_0, though there is usually little difficulty in obtaining a sufficiently accurate value of y_m. The values of y_m obtained from different sets of comparable data are found, in fact, to agree very closely.

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ULTRA-VIOLET BAND SYSTEMS OF GeSe AND GeTe, AND THEIR RELATIONS TO THOSE OF SIMILAR MOLECULES

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ABSTRACT. The production of ultra-violet band systems of two of the three group-IV(b)+group-VI(b) molecules which remained to complete the authors' investigations in this series, viz., GeSe and GeTe, is described. They are obtained in emission in silica discharge tubes of the type successfully used in previous work. The bands are degraded to the red, and show strong vibrational isotope effect. About 24 band heads have been measured and assigned to a GeSe system lying in the region λ3170–λ3570, while a number of weakly developed bands in the region λ3060–λ2660 which may belong to a second GeSe system have been measured, but not analysed. 29 bands lying between λ3380 and λ3830 are assigned to the GeTe system. Band heads of the systems are represented by the equations

(i) GeSe. $\nu_{\text{head}} = 30431{\cdot}9 + (272{\cdot}4u' - 1{\cdot}05u'^2) - (406{\cdot}8u'' - 1{\cdot}2u''^2)$,

(ii) GeTe. $\nu_{\text{head}} = 27969{\cdot}5 + (219{\cdot}4u' - 1{\cdot}3u'^2) - (323{\cdot}4u'' - 1{\cdot}0u''^2)$,

where $u = v + \frac{1}{2}$.

As a result of this work, ground-state data are available for 19 of the 20 molecules of the group, and a fairly complete discussion of the behaviour of the vibrational constants is made possible. The vibrational frequencies, force constants, energies of dissociation and internuclear distances are considered in turn, and the homogeneity of the group is established to a remarkable degree. Unfortunately the same cannot be said of the upper states of these molecules, data on which are still inadequate in many directions.

§ 1. INTRODUCTION

A RECENT series of investigations has had as its chief object a comparative study of the vibrational coefficients of the ground states and of analogous excited electronic states of the twenty diatomic molecules MX, where M is a group-IV (b) atom, and X a group-VI (b) atom. On account of their refractory nature and their chemical properties many of these substances required special means for the production of their spectra either in emission or in absorption. The ultra-violet band system of SiS, the first to be studied by the present authors⁽¹⁾, was produced in emission by a heavy-current uncondensed discharge either through silicon monosulphide itself, or through aluminium sulphide, in a silica tube. An analogous method has since been used for the production of the ultra-violet systems of SiSe and SiTe⁽²⁾, and SnTe⁽³⁾. The application of this method to the production of the GeSe and GeTe spectra is described in the following pages.

In addition to this, the earlier data for CSe, which were few and rather rough, have been replaced by new(4), and the constants derived from the SnO data have be re-examined(5). As a result of this work (on molecules which would probably have been regarded as insufficiently important for investigation had it not been considered desirable to obtain data for at least one pair of electronic states of every molecule of a large chemical group), the study of the molecular constants, which began with an investigation of the ultra-violet system of GeO(6), can now be carried to a stage much nearer to completion than appeared to be possible at the time of the work on SiS. The new data, however, have revealed serious limitations in our knowledge of the correlation of the excited states of certain of these molecules, and the lack of accurate values for some of the energies of dissociation, even in the ground states. The need for further experimental work, especially on emission by the molecules whose spectra have as yet been studied only in absorption, has been emphasised(3) ; this work has been temporarily discontinued owing to the war.*

§ 2. EXPERIMENTAL

In the work on SiS(1) it was shown that this substance could be prepared *in situ* in a suitable silica discharge tube (figure 3 (1)), by means of the reactions expressed in the equations

$$2Al_2S_3 + 3SiO_2 = 2Al_2O_3 + 3SiS_2$$
$$2SiS_2 = 2SiS + S_2,$$

which had previously been used by Thiede and Thimann(8) for the preparation of the sulphides of boron, silicon, lead and zinc. This suggested that the corresponding reactions in which selenium and tellurium, respectively, replaced sulphur in these equations would proceed with an equal, if not greater, readiness under similar conditions. This is actually the case, and the production of SiSe and SiTe by means of this reaction is entirely successful. Since, however, silicon compounds and their band systems are produced so readily, it was feared that they would be necessary and unavoidable accompaniments of a discharge through any such reaction mixture in a silica tube, and that investigations of other than silicon compounds would be hampered by the presence of these impurities. Fortunately, in the presence of a slight excess of aluminium powder, there is a reaction between the aluminium or its oxide and the wall of the silica tube to form a very inert lining, which is presumably an aluminium silicate. The occurrence of this reaction has enabled the spectra of CSe, GeSe, GeTe and SnTe to be excited in silica tubes, in the absence of the spectra of SiSe and SiTe respectively. No systems attributable to group-VI (b) compounds of Al have been observed in these discharges; this is to be expected, as they should lie considerably to the red of the regions photographed in our present experiments.

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* One experimental plate of GeS in emission was taken in the summer of 1939. Although not entirely suitable for measurement, since the ultra-violet system of SiS is also present, several new bands of the GeS system have been recorded(7) towards the long-λ end of the plate where it is free from SiS ; this observation alone about doubles the number of vibrational levels recorded in the ground state.

For the production of the spectra of GeSe or GeTe, a powdered mixture of germanium dioxide, aluminium, and selenium or tellurium has been used, with air as the residual gas. In these discharges an excess of metallic aluminium serves the additional function of a getter for the removal of residual nitrogen. It may be noted that this process of excitation is very efficient as regards consumption of material. The grating spectrograms of GeSe and GeTe reproduced in the plate (figure 1) were taken with a total consumption of only 0·5 g. of germanium dioxide. The current through the tube was limited to about 2 amp. It was taken from a 2400-v. 5-kva. transformer whose primary was supplied with 50-c./sec. A.C. from the 230-v. mains. The spectrograms were taken on Ilford Ordinary and Zenith-650 plates in a first order of a 2·4 m. concave grating in an Eagle mounting, the dispersion being about 7·4 A./mm. and the times of exposure varying from 5 to 10 minutes.

The ease of excitation of the band systems involving the elements of low atomic number in this group is remarkable. CO and CS have long been known to be extremely persistent impurities in discharge tubes: at the high temperatures of our silica tubes, these compounds readily disappear from the positive column, where, in the absence of a sufficient excess of aluminium, the corresponding silicon compounds take the place of CO and CS as readily excitable impurities. The relative intensities of two competing band systems are dependent on a number of factors, the vapour pressures of the emitting molecular species, the shapes of their potential-energy curves for the excited states etc., and are therefore dependent on the pressure and other conditions of excitation. It is, however, surprising that in our experiments, using Se and Te probably containing less than 0·1 per cent S, the ultra-violet systems of CS at low temperatures, and SiS at high temperatures, were, in the absence of a sufficient excess of aluminium, developed with an intensity of the order of one-tenth of that of CSe⁽⁴⁾ and GeTe respectively, although the ratio of the molecular concentrations of the latter compounds to the former was certainly greater than 500 : 1.

§ 3. VIBRATIONAL ANALYSIS AND ISOTOPE EFFECTS

The band systems attributed to GeSe and GeTe consist of red-degraded bands in the regions λ3170–λ3570 and λ3380–λ3830 respectively, and are shown in the enlarged spectrograms in the plate (figure 1). It will be seen that in each case the heads near the middles of the systems are fairly sharp, while those of the outer bands become increasingly diffuse as the distances from the centres increase. A short discussion of this isotope effect appeared in the paper on SnTe⁽³⁾, and the effect for the present molecules is so similar that very little need be stated here. The *International Table of Stable Isotopes* (1936)⁽⁹⁾ shows 5, 6 and 7 isotopes of Ge, Se and Te respectively. Accordingly there are no fewer than 30 isotopic

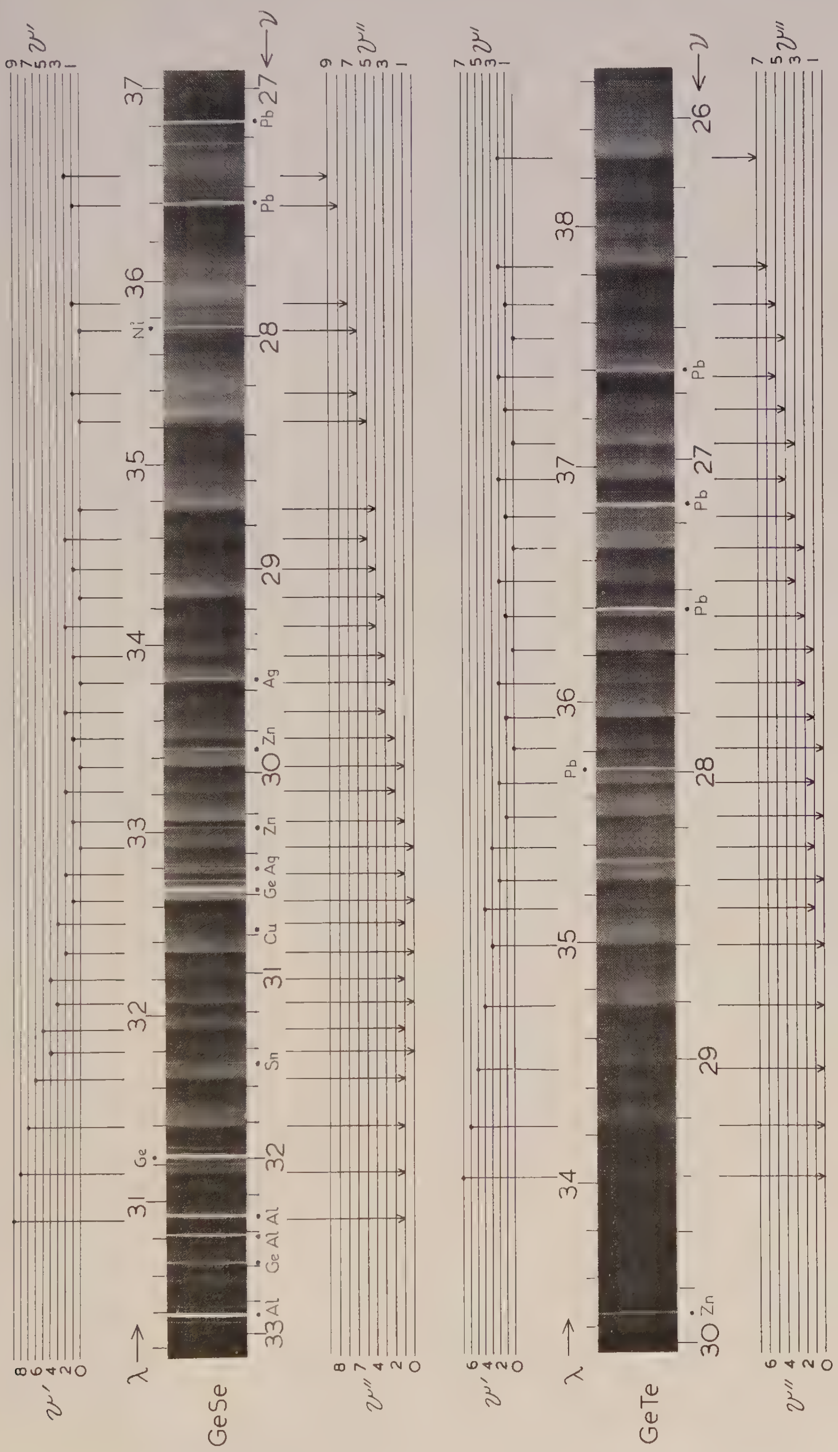

Figure 1. Ultra-violet band systems of GeSe and GeTe (2·4-m. grating, first order).

molecules of GeSe and 35 of GeTe. These numbers are reduced to 17 and 17 if we ignore abundances of 10 per cent and less. For GeSe, a diagram in which vertical lines of height proportional to intensity are spaced on a horizontal scale of coefficients $(\rho-1)$ of vibrational displacement from the band head due to the most prominent molecule is given in figure 2 (i). This shows four intensity maxima (*a*), (*b*), (*c*) and (*d*), the separations of (*b*), (*c*) and (*d*) from (*a*), that due to the most abundant molecule ^{74}Ge^{80}Se, being about $0{\cdot}007\,(\nu-\nu_e)$, $0{\cdot}014\,(\nu-\nu_e)$ and $0{\cdot}020\,(\nu-\nu_e)$, which are roughly the calculated displacements for ^{72}Ge^{80}Se,

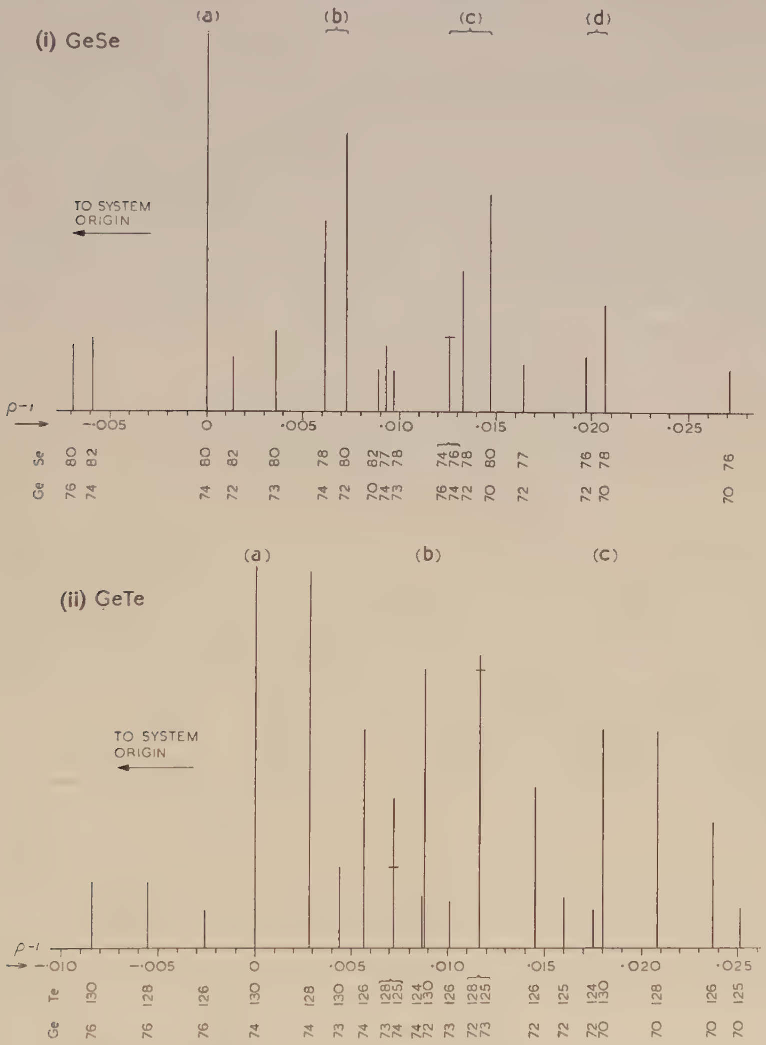

Figure 2. Theoretical isotope effect in (i) a GeSe band, (ii) a GeTe band. Intensities below 10% of the intensity of (*a*) are omitted.

^{70}Ge^{80}Se and ^{70}Ge^{78}Se respectively. In a similar diagram, figure 2 (ii), for a composite band of GeTe the stronger heads are seen to occur at small intervals of about 0·003 $(\nu-\nu_e)$, since each of the well-spaced heads (*a*), (*b*) and (*c*) due to the Ge isotope effect, about 0·009 $(\nu-\nu_e)$ apart, is accompanied by an almost equally strong head at a distance of 0·0028 $(\nu-\nu_e)$ and a weaker head at 0·0056 $(\nu-\nu_e)$, both due to the Te isotope effect. In addition to these main features, the isotopes of lower abundance have the effect of producing a diffuse background against which the maxima appear as blends, except, in general, in the favourable case of a strong band on the low-ν side of the origin. It has not been found possible to measure these maxima, except in a few of these favourable bands, but this failure is of little consequence, since all the essential facts of the isotope effect are now well established. It is, however, reasonably certain that the bands set out in Deslandres schemes in tables 1 and 2, near the respective system-origins at least, relate to the most abundant molecules ^{74}Ge^{80}Se and ^{74}Ge^{130}Te. These bands, near the system-origins, have been given the greatest weight in the derivation of the vibrational constants.

Table 1. GeSe band-head data

Italics denote wave-lengths in air (I.A.);
Large Roman, wave-numbers *in vacuo* (cm.$^{-1}$);
Small Roman, wave-number differences.

↑ v' \ v''→	0		1		2		3		4		5		6
6			31529 *3170·8*										
			244										
5			31285 *3195·4*										
4	31430·9 *3180·67*												
	264·0												
3	31166·9 *3207·61*												
	264·8												
2	30902·1 *3235·10*	405·5	30496·6 *3278·12*	408·5	30088·1 *3322·62*	385·9	29702·2 *3365·79*	397·0	29305·2 *3411·39*	397·0	28908·2 *3458·18*		
	264·4		263·2		258·4		266·3		257				
1	30637·7 *3263·01*	404·3	30233·4 *3306·65*	403·7	29829·7 *3351·41*	393·8	29435·9 *3396·24*	388	29048 *3441·6*				28252·4 *3538·53*
	270·2		270·7		270·4		269·8		274				269·3
0	30367·5 *3292·05*	404·8	29962·7 *3336·53*	403·4	29559·3 *3382·12*	393·2	29166·1 *3427·66*	391·8	28774·3 *3474·33*	393·1	28381·2 *3522·46*	398·1	27983·1 *3572·57*

Table 2. GeTe band-head data

Italics denote wave-lengths in air (I.A.);
Large Roman, wave-numbers *in vacuo* (cm.$^{-1}$);
Small Roman, wave-number differences.

↑ v′	v″→0		1		2		3		4		5		6
8	29583 *3379·3*	325	29258 *3416·9*										
	195		203										
7	29388 *3401·8*	333	29055 *3440·7*										
	196		184										
6	29192 *3424·6*	321	28871 *3462·8*										
	214												
5	28978 *3449·9*												
	213												
4	28765·4 *3475·41*	321·4	28444·0 *3514·68*										
	202·0		200·6										
3	28563·4 *3499·98*	320·0	28243·4 *3539·65*										
	213·3		213·4										
2	28350·1 *3526·33*	320·1	28030·0 *3566·59*	325·5	27704·5 *3608·50*	315·7	27388·8 *3650·09*	318·6	27070·2 *3693·05*	319	26751 *3737·2*		
	216·4		216·3		212·1				212·5		205		
1	28133·7 *3553·44*	320·0	27813·7 *3594·33*	321·3	27492·4 *3636·34*				26857·7 *3722·27*	312	26546 *3766·0*	304	26242 *3809·7*
	217·6		217·0		216·2				215·1		210		
0	27916·1 *3581·14*	319·4	27596·7 *3622·59*	320·5	27276·2 *3665·16*	317·2	26959·0 *3708·28*	316·4	26642·6 *3752·32*	307	26336 *3796·0*		

About 23 bands have been attributed to GeSe, and in many of them more than one head has been measured. The expression derived from these measurements is

$$\nu_{\text{head}} = 30431{\cdot}9 + (272{\cdot}4u' - 1{\cdot}05u'^2) - (406{\cdot}8u'' - 1{\cdot}2u''^2),$$

where u' and u'' are written for $(v' + \frac{1}{2})$ and $(v'' + \frac{1}{2})$.

The corresponding expression for GeTe, in which some 30 bands have been measured, is

$$\nu_{\text{head}} = 27969{\cdot}5 + (219{\cdot}4u' - 1{\cdot}3u'^2) - (323{\cdot}4u'' - 1{\cdot}0u''^2).$$

Besides the bands included in tables 1 and 2, the following have also been observed:

(1) In discharge through Al, GeO_2 and Se: the AlCl system near λ2610, and the heads listed in table 3: these may possibly belong to a second system of GeSe, but the measurements of these weakly developed bands are insufficiently accurate to justify an attempt at vibrational analysis.

(2) In discharge through Al, GeO_2 and Te: the AlCl system near λ2610, and, in the region λ2730–λ3060, a weak development of the main bands of the SiS and SiSe ultra-violet systems.

Table 3. Heads of ultra-violet bands, degraded towards the red, observed beyond the band system of GeSe, in discharge through GeO_2, Al and Se.

Intensity	λ_{air}	$\nu_{vac.}$	Intensity	λ_{air}	$\nu_{vac.}$
?2	3057·1	32071	2	2839·5	35207
?1+	3017·9	33126	2+	2823·7	35404
?1−	3010·4	33208	2	2806·4	35622
1	2981·3	33533	2	2791·4	35814
1−	2949·6	33893	2	2775·7	36016
1	2936·2	34048	1+	2760·0	36221
?2	2922·9	34203	1	2744·4	36427
2	2918·4	34255	1	2730·9	36607
2	2905·7	34405	1−	2715·1	36820
2+	2890·1	34591	0	2701·1	37011
2	2888·0	34616	0	2687·5	37212
?2−	2876·3	34757	0	2672·5	37407
1	2869·7	34837	0	2670·3	37438
2	2855·2	35014	?0	2657·7	37615

§ 4. DISCUSSION

Table 4, in which the symbols are those ordinarily used, gives data for the ground states of nineteen of the twenty molecules of this group, the molecule for which no spectrum has yet been observed being CTe. It is to be noted that the states of CSe, SiSe, SiTe, GeSe, GeTe and SnTe are here assumed to be ground states. In view of the close similarity between systems involving these states and those of the remainder of the molecules of the group, already known to involve the ground states, this assumption is probably justified, but confirmation by means of absorption experiments is, of course, desirable. It is not proposed to include the excited electronic states in this brief survey, as the correlation of these states among the different molecules of the group is by no means certain. Empirical rules concerning the behaviour of the vibration frequencies (1), (12) and of the electronic energies (3) have been suggested as possible bases for schemes of classification and, in particular, the latter quantity appears to vary with the atomic ionization potentials in a manner which may be significant (13). But, in view of the present uncertainty as to the molecular configurations obtaining in many of these states, the tentative nature of certain of the postulated systems

Table 4. Constants for ground states

n	Molecule	$\mu\times10^{24}$ (g.)	ω_e'' (cm.$^{-1}$)	$x_e''\omega_e''$ (cm.$^{-1}$)	D_0'' (ev.)	r_e'' (A.)
14	CO	11·31	2168·2	13·04	9·144*	1·1284
22	SiO	16·80	1242·0	6·05	7·4	1·510
40	GeO	21·62	985·7	4·30	6·9	1·647
58	SnO	23·25	822·4	3·73	5·7	1·838
90	PbO	24·48	721·8	3·70	4·3	1·923
22	CS	14·40	1285·1	6·50	7·8	1·536
30	SiS	24·68	749·5	2·56	6·7	(1·88)§
48	GeS	36·67	575·8	1·80	5·6	(2·11)
66	SnS	41·62	487·7	1·34	5·0	(2·27)
98	PbS	45·76	428·1	1·20	5	2·395
40	CSe	17·19	1036·0	4·8	6·8	(1·65)
48	SiSe	34·16	580·0	1·78	5·8	(2·10)
66	GeSe	62·46	406·8	1·2	4·1	(2·50)
84	SnSe	78·32	333·2	1·25	2·7	(2·81)
116	PbSe	94·43	277·8	$0{\cdot}4_5$	—	(3·18)
58	CTe	18·10	(1000)†	(4·3)†	(7·2)†	(1·67)
66	SiTe	37·92	480·4	1·61	5·5‡	(2·29)
84	GeTe	76·27	323·4	1·0	3·2	(2·85)
102	SnTe	101·3	263·7	1·1	1·9	(3·29)
134	PbTe	130·2	211·8	$0{\cdot}1_2$	—	(4·05)

Notes to table 4:

* The value 6·921 ev. is not excluded with certainty(10), (11).

† Values interpolated from figures 4 and 6.

‡ This figure corrects one given in a previous paper(2).

§ Values of r_e'' in parentheses have been interpolated from figure 7: other values from Herzberg(14).

involving transitions between them, and the probability that some of these molecules possess excited states as yet uninvestigated, it is scarcely possible to draw any useful conclusions from the behaviour of their vibrational constants. It can only be said that one is able to select certain excited states for which the vibrational constants exhibit variations which are quite parallel to those observed among the ground-state constants.

Vibration frequencies

In the paper on SiS (1) it was shown that when $1/\omega_e$ was plotted against n a family of smooth uninflected curves was obtained for the oxides, sulphides, selenides and tellurides, and for these compounds of C, Si, Ge, Sn and Pb. The additional data which have appeared since then confirm their general character, as is evident from figure 3, (i) and (ii).

The vibration frequency, according to the equation

$$\omega = 1/2\pi \,.\, \sqrt{(K/\mu)},$$

exhibits a variation with the reduced mass, although the variation is not a simple one, as the force constant, K, itself tends to diminish with increasing atomic number. The behaviour of the vibration frequencies of these molecules is shown in figure 4, where values of log ω_e'' are plotted as ordinates against log μ as abscissae, and the graph gives a semi-quantitative expression to the expected decrease in vibration frequency with increase in mass of the molecule. It may be noted that a similar curve is found when $1/\omega_e$ is plotted against log μ. In both cases, however, the irregularities are outside the limits of error of wave-length measurement and are evidently significant. Apart from the general trends observed in

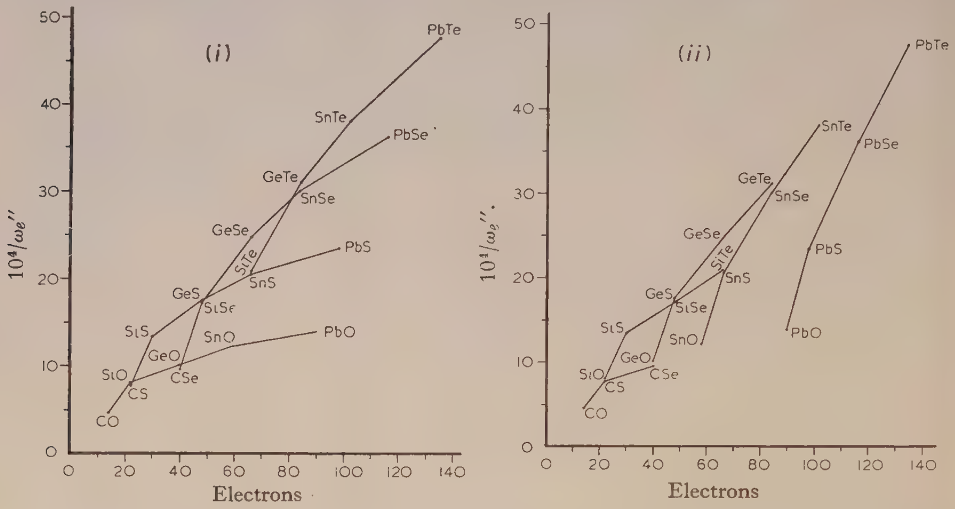

Figure 3. Reciprocal of vibrational frequency in the ground state as a function of the electron number. Consecutive points are joined by straight lines to show the trend (i) through group IV(b) for each group-VI(b) atom, and (ii) through group VI(b) for each group-IV(b) atom.

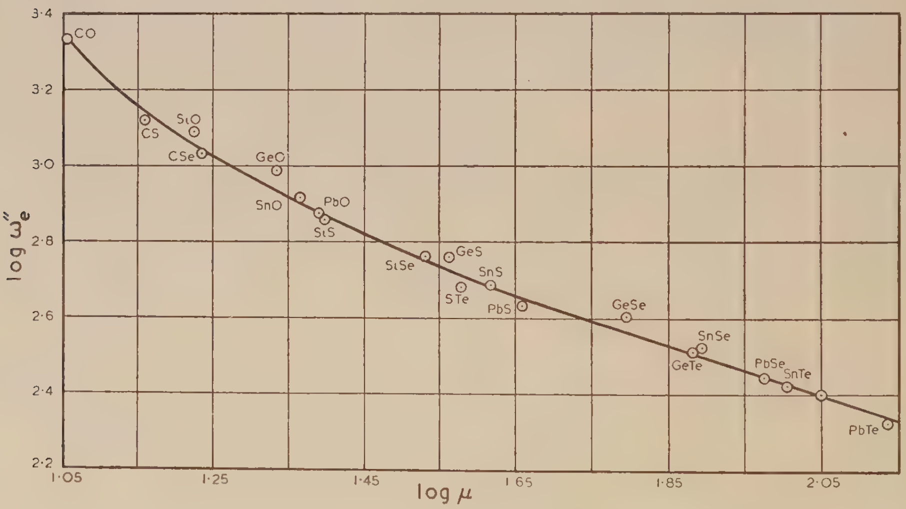

Figure 4. Log ω_e'' as a function of log (reduced mass).

these graphs, the vibration frequencies are not, in view of their close dependence on mass, as suitable for the unravelling of periodic relations as the force constants K, defined in the equation above. These may be expected, perhaps, to be more sensitive to changes in electronic structure and nuclear shielding than the vibration frequencies. The quantity chosen to express numerically the electronic structure of the component atoms is the product of the ionization potentials, $I_M I_X$, against which values of the force constants are plotted in figure 5. The close approximation to linearity of the graphs for the compounds of C, Si, Ge, Sn and Pb, and the similarity of the slight departures from the straight line in each case (the selenide point lying a little high, the telluride a little low) indicates the possibility of a periodic correlation between the two quantities. At the same time it is not clear why the graphs through the points for the oxides, sulphides, selenides and tellurides, respectively, should not also be approximately linear, although the anomaly might be at least partly explained by errors in the values accepted for the ionization potentials of Si and Pb.

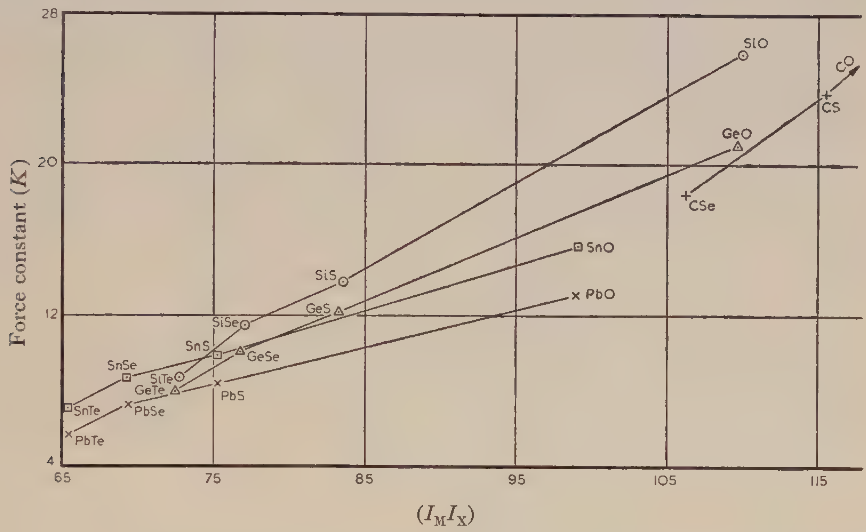

Figure 5. Force constant (K) as a function of the product of the atomic ionization potentials I_M and I_X, each of which is expressed in ev. Consecutive points are joined by straight lines to show the roughly linear variation through group VI(b) for each group-IV(b) atom. The point for CO lies off the diagram in the direction of the arrow from CS; its inclusion would reduce the scale unduly.

Energies of dissociation

A general decrease in the energy of dissociation with increasing molecular weight is to be expected in a group of homologous molecules, where the atomic products of dissociation are all in the ground states (in the present group ^3P states). At the time of the publication of the paper on SiSe and SiTe(2), the values of D_0''

were such that no general trend of this kind could, in fact, be observed. In figure 6, D_0'', which is obtained by linear extrapolation using the expression

$$D_0 = (\omega_e - x_e\omega_e)/4x_e\omega_e \times 8106,$$

is plotted against μ. The graph indicates that there is a surprisingly close relation between these quantities, the energy of dissociation decreasing, after rather a sharp initial fall, almost linearly with increasing reduced mass. Certain of the values fall far off the curve, e.g., those for SnO and PbO, but these large departures seem to be due to inaccurate determinations of $x_e''\omega_e''$, which are based on absorption experiments, and, consequently, on an insufficient number of vibrational levels in the ground state, or on measurements inaccurate on account of complicated isotope effects. (It is probable that such inaccuracies are responsible for the dissimilarity of behaviour of the dissociation energies of the Si and Pb compounds to which attention was drawn in a previous paper⁽²⁾.) It may indeed be suggested that more accurate values of $x_e''\omega_e''$ than are now available for such molecules as SnO and PbO may be obtained by interpolation from figure 6. It seems at present impossible to give any quantitative interpretation of the relation between D_0'' and μ, but we may note that the direct relation suggested by figure 6 is hardly to be expected, as μ is merely a function representing the variation of electronic shielding of the nucleus. The graph which might perhaps have been expected to show more clearly this relation, namely that of D_0'' against $I_M I_X$, although exhibiting the gradual weakening of the bond with decreasing $I_M I_X$, is by no means of such simple form as that shown in figure 6.

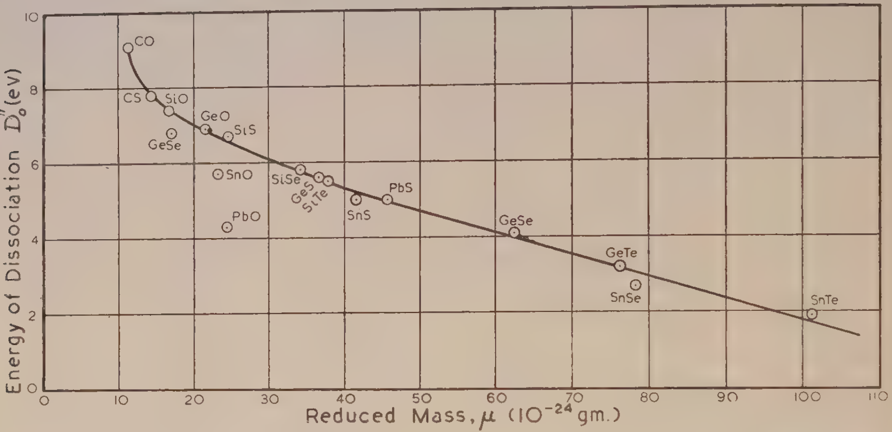

Figure 6. The variation of the energy of dissociation of ground state with reduced mass.

Internuclear distances

In figure 7, Morse's relation, $\omega_e r_e^3 = \text{constant}$, is tested for those molecules whose r_e values are known. With the single exception of CO, which is irrelevant for interpolation purposes, the rule holds remarkably well; thus the error in r_e for SiO, the least satisfactory point on the line, is less than 3 per cent. Values of r_e'' for those molecules whose band systems are yet to be analysed rotationally are therefore included in parentheses in table 4. Other and more accurate empirical expressions for r_e have been developed recently (for references see Clark and Stoves[(15)]), but they are not considered here, since they require discussion of constants which are sensitive not only to changes in the group of the periodic

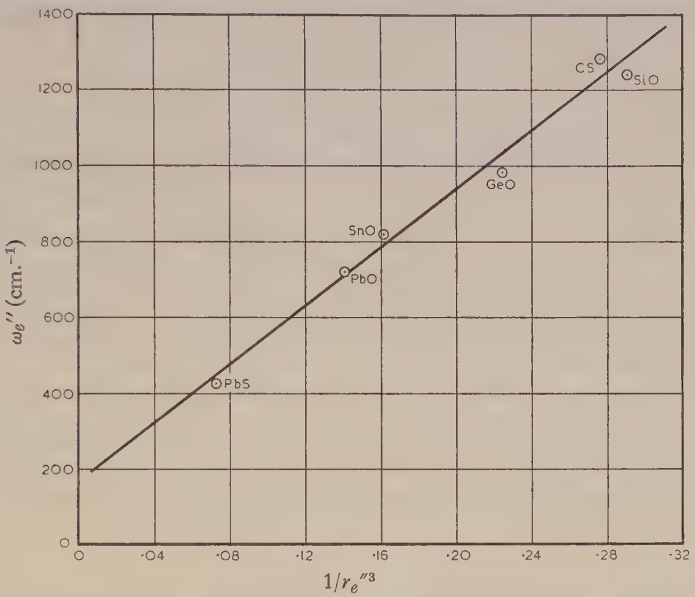

Figure 7. The vibration frequency as a function of $1/r_e^3$ for ground states: a test of Morse's rule. The point for CO is omitted; it lies rather far off the straight line, and in any case, there are no molecules in the group taking ω_e'' values between that for CO and that for CS, which is on the graph.

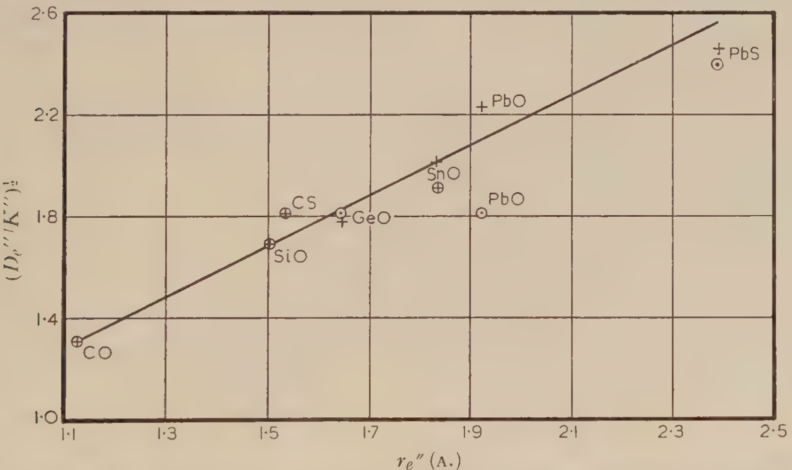

Figure 8. $(D_e/K)^{\frac{1}{2}}$ as a function of r_e: a test of Sutherland's relation. Points labelled ⊙ correspond to the values of D_0'' given in table 4, obtained by the use of Morse's extrapolation rule: points labelled + correspond to smoothed values of D_0'' taken from figure 6.

table to which the atoms comprising the diatomic molecules belong, and to the electron configuration, but also to changes in the horizontal periods involved.

Sutherland, in a recent paper (16), by assuming a potential function of the form

$$U = -\alpha/r^m + \beta/r^n,$$

obtains the expression

$$D_e = k_e r_e^2/mn.$$

The curves for $(D_e k_e)^{\frac{1}{2}}$ against r_e for molecules in the same horizontal periods of the periodic table approximate to straight lines, indicating that mn is a constant quantity for each series of such molecules tested; an "effective" internuclear distance $r_e - d_{ij}$ requires to be used. He also finds that satisfactory straight lines can be drawn connecting molecules of related elements, e.g., O_2, S_2, Se_2 and Te_2, and HF, HCl, HBr and HI. When this test is applied, as in figure 8, to those molecules of the present group whose r_e values are known, a straight line is found passing nearly through the origin; for SnO, PbO and PbS, smoothed values of D_e from figure 6 are more appropriate than those from the Morse extrapolation using the present vibrational data. As Sutherland remarks, the reason for the approximately linear relation between $(D_e k_e)^{\frac{1}{2}}$ and r_e among molecules related vertically in the periodic table is not at present clear.

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THE VARIATION OF SPARKING POTENTIAL WITH INITIAL PHOTO-ELECTRIC CURRENT

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ABSTRACT. The minimum sparking potential of a discharge-gap is known to be lowered appreciably when the cathode of the gap is subjected to the *intense* ultra-violet radiations produced by an auxiliary spark-gap. This lowering is ascribed to the field distortion produced by the positive space-charge formed in the gap as a result of the difference in mobilities of positive ions and electrons, and is explained in terms of the writer's theory of spark discharge. Calculations are made on such a basis for a steady initial photo-electric current and give values for the lowering in reasonable agreement with experiment when it is noted that in all experiments so far performed the source of illumination is a transient one, far shorter in duration than the time to establish the equilibrium space-charge calculated. The time lag of sparking for large initial currents is shown to be related to the time of build-up of the space-charge field, and its variation with applied potential and initial current is indicated.

§1. INTRODUCTION

The static sparking potential of a uniform-field discharge-gap has been observed to be independent of the intensity of ultra-violet illumination over a considerable range of values. Relatively recently it has been found to be lowered appreciably when the cathode of the gap is subjected to the intense radiations produced by a condensed spark. The lowering as observed by White(1) for a 5-mm. gap at atmospheric pressure was as much as 10 per cent. Subsequent measurements by other workers(2) have confirmed White's original experiments. In all cases the source of illumination was an auxiliary spark-gap, while the variation of intensity was obtained by a change in distance between the source and the gap under observation or by absorbing screens. The equivalent value of the photo-electric current, i_0, was obtained by measurements of the number of photo-electrons released at the cathode, and by assuming the duration of the spark to be $\sim 10^{-4}$ sec. Clearly such an estimate of i_0 is inaccurate, and may be meaningless except in so far as it might give a limiting order of magnitude; for i_0 varies with time in the passage of a single spark, and several flashes may occur in a condensed discharge when the circuit is not critically damped. No measurements appear to have been made with steady sources of illumination (e.g., the quartz-mercury arc) giving values of i_0 much higher than about 10^{-13} amp. per cm^2 of cathode.

On the basis of the Townsend theory of spark discharge, Rogowski and Wallraff (3) have shown that the lowering of the sparking potential with increasing i_0 may be accounted for by the presence of a space-charge field produced by positive ions in the gap as a result of the large difference in mobility between the electrons and positive ions. Calculations gave a semi-empirical relation, which, by adjustment of constants and an assumed variation of ion mobility, could be made to approximate to the observed experimental data. However, since there is now much evidence that the Townsend theory is not applicable except at low pressures and short gap-lengths, one must consider that the variation of sparking potential with i_0 is still not satisfactorily explained.

An alternative theory to that of Townsend for spark discharge was qualitatively suggested by Loeb (4) and has been put on a quantitative basis by the writer (5). This new theory is based on electron multiplication and photo-ionization in the gap, and is applicable to discharge-gaps in which the product pd of pressure and gap length is greater than about 200 mm. Hg × cm. Below this value of pd, cathode-dependent secondary mechanisms become active and the Townsend theory has been shown to hold. The theory further enables the development of an equation from which the minimum sparking potential of a gap of length d cm. at a pressure p mm. Hg can be determined, viz.,

$$\alpha d+\log_e \alpha/p=14{\cdot}46+\log_e X/p+\tfrac{1}{2}\log_e d/p \qquad \ldots\ldots(1),$$

where α is the first Townsend coefficient for ionization by electrons, which corresponds to the sparking field-strength X volts per cm. This equation can be solved for particular values of d and p from a knowledge of the curves which relate α/p and X/p.

The effect of i_0 on the value of the sparking potential of a given gap will now be considered on the basis of the writer's theory of spark discharge. As in the case of Rogowski and Wallraff's work, the primary cause of the lowering of sparking potential with increasing i_0 is ascribed to the effect of the antecedent positive-ion space-charge and the consequent variation of field in the gap.

§ 2. THEORY

In the original derivation of the theory proposed by the writer for spark discharge in air at atmospheric pressure no statement is made about the value of the initial photo-electric current necessary to initiate the spark. It only requires that one electron shall cross the gap under such a propitious chain of circumstances that the field produced by the positive-ion space-charge in the electron avalanche, together with photo-ionization in the gas, shall succeed in the production of a streamer which develops from anode to cathode. Near the sparking threshold the statistical fluctuations in the avalanche processes may make the achievement of a successful streamer-producing avalanche a relatively rare occurrence. Hence for a given applied potential many photo-electrons may need to pass before a spark occurs. An increase in the value of i_0 then increases the chance of a spark at a lower value of the applied potential V_s. Thus the observed sparking potential can appear to vary with i_0, i.e., the higher i_0, the more likely that sparks will occur for the lower values of V_s(6).

This uncertainty in the value of V_s and the dependence on i_0 indicate that there is some latitude in the value of the radial field-strength generated by the positive space-charge in the avalanche, relative to the impressed field under which a spark will pass with varying circumstances. Thus the theoretical criterion for the passage of a spark is by its nature somewhat indefinite. However, as a consequence of the rapid rise of α/p as a function of X/p, and the exponential character of ionization by collision (7), the considerable spread of possible ionizing events which could lead to a spark will be confined to a narrow region of field-strength X, e.g. for a 1-cm. gap in air at atmospheric pressure, $X_s = 32\,200$ volts per cm. for the condition: radial field-strength $X_1 = X_s$, while $X_s = 31\,800$ volts per cm. for the condition: $X_1 = 0{\cdot}2X_s$. Thus we may have an illusion as to the existence of a definite sparking-potential threshold.

The actual sparking potential as conventionally observed for a given initial illumination of cathode is determined by the frequency of sparking which conforms to the observer's patience in the rate at which the measuring potential is raised. This leads to a rather indeterminate value of the sparking potential as witnessed by the variable results achieved by different workers. On account of the reasons given above, the observed range is fairly narrow, and recent work in this laboratory by Haseltine (8) indicates that within this range the sparking potential is exceedingly ill defined.

The new theory, as originally stated (5), only envisaged minor statistically conditioned alterations of the sparking potential. However, when one considers a spark-gap in which there is a heavy initial photo-electric current, it is possible that a positive space-charge field distortion may build up owing to the relative mobilities of electrons and positive ions before a spark occurs. The existence of such space-charge distortions was early indicated by Loeb (9) and Rogowski (10) independently as a means by which the second Townsend coefficient would be altered in such a way as to increase the ionization and thus to enhance the field distortion further. Analyses along similar lines were later made by other authorities (11) in order to account for the sparking potentials observed on the basis of the Townsend mechanism of ionization by positive ions. That such space-charge distortions actually occur in the Townsend gaps and influence the value of the primary coefficient α in the gap was first shown by Posin (12). The rigorous theory for the evaluation of the steady-state field-distortion under the ordinary experimental conditions was set up and solved by Varney and his co-workers (13). It was shown that these distortions would lead to a spark for an adequate gap-length. Before such gap-lengths are reached, however, spark breakdown occurs by what we now know to be streamer formation.

The theoretically calculated potential for breakdown of a 1-cm. gap at N.T.P., as obtained from equation (1), is 32 200 volts. For this field-strength $\alpha d = 18{\cdot}6$, which is then the condition for a streamer to form in the uniform gap. If the field varies across the gap then αd must be replaced by $\int_0^d \alpha\, dx$ (5). Thus when the field is distorted by space-charge the potential now required to cause breakdown is that which, together with the space-charge field, produces such a variation of α in the gap that $\int_0^d \alpha\, dx = 18{\cdot}6$. Since the space-charge field requires time to build up, the minimum value of the external applied field occurs when the space-charge field is a maximum, i.e., after a theoretically infinite time, so that steady-state conditions virtually obtain. We will then consider the treatment of the space-charge field, as given by Varney (13), in conjunction with the streamer theory of spark discharge.

Consider two parallel plate electrodes, separated by a distance d, and with the cathode illuminated by ultra-violet light which liberates photo-electrically a current density of electrons i_0. At any plane in the gas at distance x from the cathode the electron current is given by $i = i_0 e^{\alpha x}$, where α is the electron ionization-coefficient. The current reaching the anode is $i_0 e^{\alpha d}$. Since the total current crossing any plane parallel to the electrodes must be constant under steady-state conditions, the positive ion current is given by $i_+ = i - i_- = i_0\,(e^{\alpha d} - e^{\alpha x})$.

The variation of field in the gap is given by Poisson's equation

$$\frac{\partial X}{\partial x} = -4\pi(\rho_+ - \rho_-),$$

where ρ_+ and ρ_- are the densities of positive ions and of electrons respectively. Since $i = \rho v = \rho k X$, where v = velocity, k = mobility ($k = 1{\cdot}6$ cm. per sec./volt per cm. for positive ions at N.T.P.), we obtain

$$\frac{\partial X}{\partial x} = -\frac{4\pi}{X}\left[\frac{i_+}{k_+} - \frac{i_-}{k_-}\right]$$

$$= -\frac{4\pi i_0}{X}\left[\frac{e^{\alpha d} - e^{\alpha x}}{k_+} - \frac{e^{\alpha x}}{k_-}\right],$$

where i_0 is the current density. Since k_- is about 300 times k_+, $1/k_-$ may be neglected with respect to $1/k_+$, so that

$$X\frac{\partial X}{\partial x} = -\frac{4\pi i_0}{k_+}\left[e^{\alpha d} - e^{\alpha x}\right]$$

Now α/p is a function of X/p, and since X is not uniform across the gap when the field is distorted by space-charge, we should therefore write $\exp\left(\int_0^x \alpha\, dx\right)$ for

$e^{\alpha x}$ and $\exp\left(\int_0^d \alpha\, dx\right)$ for $e^{\alpha d}$. Denote $\int_0^x \alpha\, dx$ by u, and $\int_0^d \alpha\, dx$ by u_d. Then

$$\partial u/\partial x = \alpha,$$

and

$$\alpha X \frac{\partial X}{\partial u} = -\frac{4\pi}{k_+}(e^{u_d} - e^u),$$

$$\int_X^{X_0} \alpha X\, dX = -\frac{4\pi i_0}{k_+}\int_0^u (e^{u_d} - e^u)\, du,$$

i. e.

$$\phi_{X_0} - \phi_X = \frac{4\pi i_0}{k_+}(ue^{u_d} - e^u - 1) \qquad \text{......(2)},$$

where

$$\phi_X = \int_0^X \alpha X\, dX.$$

This equation was solved by Varney for another purpose by the use of a convenient approximation for α/p as a function of X/p. A more accurate solution may be made graphically for actual values of α and X, and will be given here. The method of solution is as follows:

1. Plot the curve relating ϕ_X and X. (The values of α used here are those given by Sanders (12).)

2. Plot $f(u)$, the right-hand side of equation (2), as a function of u from $u=0$ to $u=18{\cdot}6$.

3. Take a particular value of ϕ_{X_0} and plot ϕ_X as a function of u. The curve relating X and u can then be obtained, and also the further curves X/p against u, α against u, and $1/\alpha$ against u.

4. Since $du/dv = \alpha$, a condition which must be fulfilled is that $\int_{u=0}^{u=18\cdot 6} \frac{1}{\alpha}\, du = \int_0^1 dx = 1$. Thus various values of ϕ_{X_0} must be selected until the value of $\int_0^{18\cdot 6} \frac{1}{\alpha}\, du$ as obtained from the $\{1/\alpha, u\}$ curve is equal to unity.

5. When the above condition is satisfied the potential required across the gap can be determined. For $V = \int X\, dx = \int_0^{18\cdot 6} \frac{X}{\alpha}\, du$. Thus it is necessary to plot the curve relating X/α and u and to determine the area beneath the curve between $u=0$ and $u=18{\cdot}6$.

6. To obtain the distribution of potential and the field in the gap it is necessary to find the values of x corresponding to the different values of u. Since $du/dx = \alpha$, then at u, $x = \int_0^u \frac{1}{\alpha}\, du$. Thus the values of X and x can be related and then the potential at x determined from $V = \int_0^x X\, dx$.

The values of the potential required to cause breakdown as determined from equation (2) are shown in the curve of figure 1 for values of i_0 up to 10^{-11} amp. per cm^2. The minimum sparking potential for very small i_0 ($\sim 10^{-14}$ amp.), when there is no space-charge distortion, is 32 200 volts as determined from equation (1). The potential is lowered to 31 800 volts for $i_0 = 5 \times 10^{-13}$ amp. per cm^2, i.e. a lowering of 1·2 per cent, while the lowering is 20·6 per cent for $i_0 = 10^{-11}$ amp. per cm^2

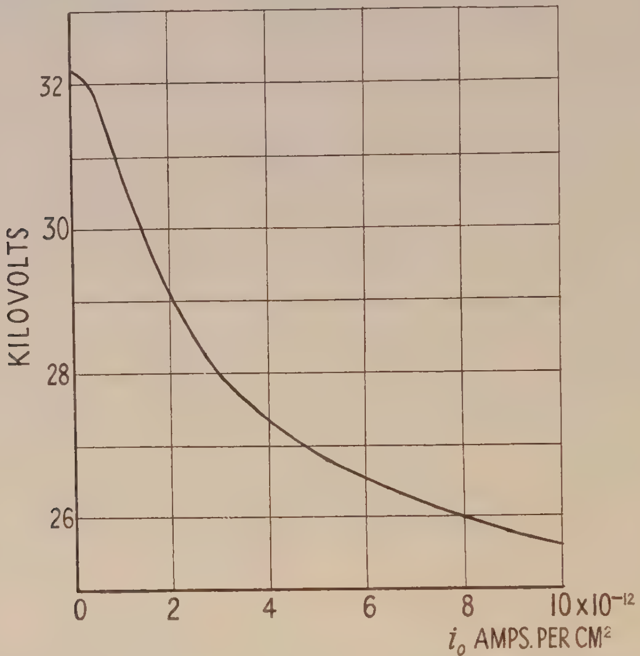

Figure 1. Curve relating the calculated minimum potential required for breakdown and the initial photo-electric current for a 1-cm. gap at N.T.P.

The distribution of potential and of field-strength in a 1-cm. gap at N.T.P. for a photo-electric current i_0 of 5×10^{-13} amp. per cm^2 has been calculated from equation (2), and the resultant curves are given in figure 2. It will be observed that the field-strength varies linearly with distance from the cathode up to the region close to the anode, where, of course, the density of electrons is high. This linear variation is of importance, in that it enables approximations to be made when the potential required to break down the gap in times of the order of 10^{-5} sec. is calculated, as will be shown in the next section.

§ 3. THE TIME OF FORMATION OF THE SPACE-CHARGE FIELD

The potential which has been determined in the previous section is that which, when applied to the gap, will theoretically cause breakdown after an infinite time. It is that which causes the space-charge field to build up so gradually that steady-state conditions may virtually be considered to obtain in the gap. In effect,

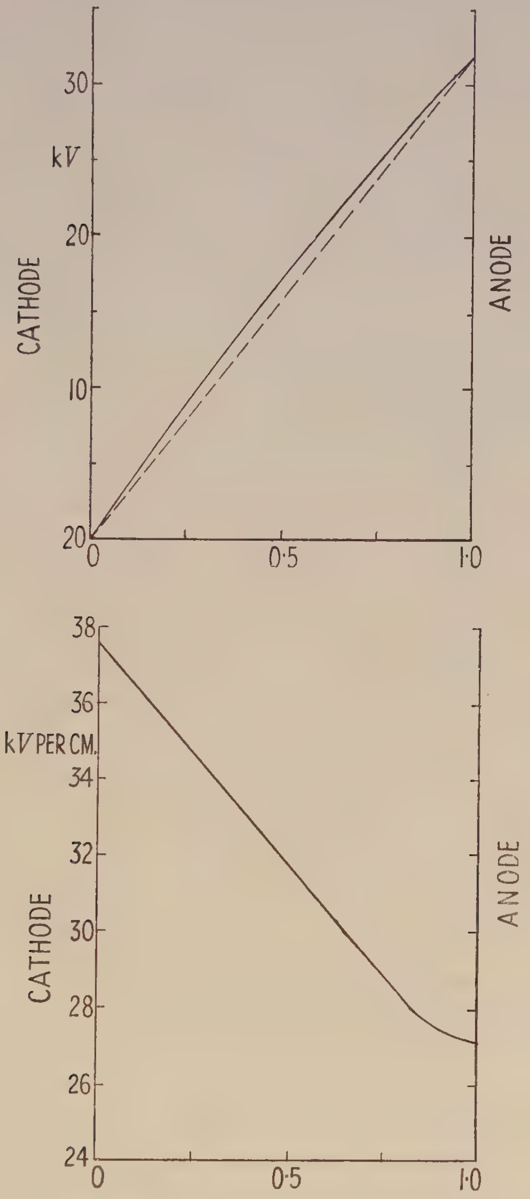

Figure 2. Curves to show (*a*) the distribution of potential, and (*b*) the distribution of field-strength, immediately previous to the breakdown of a 1-cm. gap for an initial photo-electric current of 5×10^{-13} amp. The applied potential is 31·8 kilovolts, which is the calculated minimum value for breakdown.

this probably occurs in a time of 10^{-3} to 10^{-2} sec. Now if for any particular value of i_0 a potential, V_A, is applied to the gap in excess of this minimum potential, V_M, a spark will occur after a finite time determined by the time required for the space-charge field to build up, so that $\int_0^d \alpha\,dx$ reaches the requisite value. The necessity for such a space-charge field will only occur if $V_M < V_A < V_0$, where V_0 is the potential required to give the correct value of $\int_0^d \alpha\,dx$ without any field distortion, i.e. 32 200 volts for a 1-cm. gap at N.T.P. For $V_A = V_0$ the gap will break down in a time of the order of that of electron travel across the gap ⁽⁵⁾. For values of $V_A > V_0$ this time will be further reduced as midgap streamers will form ⁽⁵⁾. However, in the region $V_M < V_A < V_0$, which is that of immediate interest in the present article, a wide variation in time of formation of the spark should be observed according to the theoretical considerations here postulated.

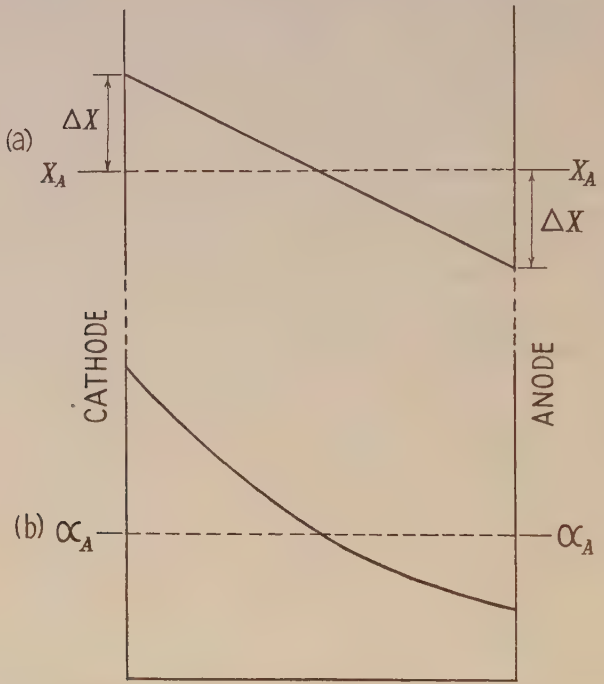

Figure 3. Schematic diagram to illustrate the approximate distribution of (*a*) field-strength, and (*b*) the first Townsend coefficient, α, in a discharge-gap where the initial photo-electric current is sufficient to lead to space-charge distortion.

In order to calculate the space-charge field required to give the necessary value of $\int_0^d \alpha\,dx$ for any particular value of V_A, and also to determine the time required for the formation of such a space-charge field, it is necessary to make certain approximations consequent on the fact that steady-state conditions do not obtain in the gap.

It has already been pointed out in connection with figure 2, that the field-strength across the gap varies linearly with distance from the cathode except for a small region close to the anode. It will here be assumed that the variation is a completely linear one from cathode to anode. Then the externally applied field-strength X_A will be increased by an amount ΔX at the cathode due to the positive space-charge in the gap, and will be decreased by the same amount ΔX at the anode, as indicated in figure 3. A further approximation is that the positive ions are all considered to occur at the anode and to travel the full gap. This is, of course, not true, but causes little error, for, owing to the exponential character of electron ionization by collision, the bulk of the positive ions are produced in a small region close to the anode. Further, it will be assumed that the density of positive ions in transit in the gap is uniform. This again is an approximation, for the ions which are about to reach the cathode will have been formed a time t sec. before those which are just leaving the anode, where t is the time of transit of positive ions across the gap, while the field will have changed during that time. Thus the density of positive ions near the anode will be slightly greater than that near the cathode, on account of the fact that the field in the gap, and therefore $\int_0^d \alpha\, dx$, has meanwhile been augmented.

The calculation of ΔX due to space-charge may be made by means of Poisson's equation. The number of positive ions leaving 1 cm^2 of the anode per second is $i_0 e^{u_1} \times 3 \times 10^9/\boldsymbol{e}$, where i_0 is the photo-electric current at the cathode in amps. per cm^2, $u_1 = \int_0^d \alpha\, dx$, and $\boldsymbol{e}$ is the electronic charge in e.s.u. The time of transit of positive ions across the gap is $t = d/v = d/k_+ X$ where $v(=k_+X)$ is the mean velocity of the ions. In these calculations it will be considered that the value of X used to determine v will be the mean value of X for the gap, i.e., $X = X_A = V_A/d$. Then the density of positive ions in the gap at any instant is

$$N = \frac{i_0 e^{u_1} \times 3 \times 10^9}{\boldsymbol{e}} \cdot \frac{d}{k_+ X_A} \cdot \frac{1}{d}.$$

The value of ΔX is then given by

$$2\Delta X = \int_0^d 4\pi\rho\, dx = 4\pi N \boldsymbol{e}\, d$$

$$= \frac{4\pi i_0 e^{u_1} \times 3 \times 10^9}{k_+ X_A} \,.\, d \quad \text{e.s.u.,}$$

or

$$\Delta X = 18\pi \times 10^{11} \frac{i_0 e^{u_1} d}{k_+ X_A} \text{ volts per cm.} \qquad \ldots\ldots(3).$$

Since $k_+ = 1{\cdot}6$ cm. per sec./volt per cm., then for a gap-length of 1 cm.

$$\Delta X = 3{\cdot}54 \times 10^{12}\, i_0 e^{u_1}/X_A \qquad \ldots\ldots(4).$$

The determination of the time lag to breakdown can now be made for any particular values of i_0 and of V_A, the applied potential. The value of V_A fixes the field-strength X_A of the original undistorted field. The original value of u_1 is αd, where α corresponds to the field-strength, X_A. On this basis the value of ΔX due to the first "wave" of positive ions which fills the gap can be determined. The distorted field gives rise to a variation of α across the gap as indicated in figure 3. From such a curve for α, the value of $\int_0^d \alpha\, dx$ can be calculated. This will give a value, u_2, greater than the u_1 above owing to the fact that X varies linearly across the gap and α increases with X in such a manner that $\partial^2\alpha/\partial X^2$ is positive.

If u_2 is still smaller than u_d, the value of $\int_0^d \alpha\, dx$ required for streamer formation, the quantity u_2 is substituted for u_1 in the expression (4) for ΔX to give a new value of ΔX. The variation of α across the gap is then again obtained, and the new value of $\int_0^d \alpha\, dx = u_3$ is determined. If u_3 is still less than u_d, the process is repeated until equality is reached. The time-lag to breakdown can then be estimated roughly by the number of successive steps required. For the time required by a single positive ion to cross the 1-cm. gap is approximately $1/k_+X \sim 2 \times 10^{-5}$ sec., where $k_+ = 1{\cdot}6$ and $X = 32\,000$ volts per cm. Then if S is the number of steps in the calculation, the time-lag to breakdown is approximately $2 \times 10^{-5}\, S$ sec.

A number of calculations have been made by the writer to determine the voltage which will cause breakdown in a time of the order of 2×10^{-5} sec. for various values of i_0. The results are given in the following table:—

i_0 (amps./cm.^{2})	10^{-14}	10^{-12}	10^{-11}	10^{-10}	10^{-8}
V (volts)	32 200	31 900	31 350	30 650	28 800

The lowering of potential is seen to be considerably less than that determined in the previous section for the corresponding values of i_0. This is, of course, to be expected, since the latter determinations assumed an infinite time for the space-charge field to build up to the requisite value, whereas in the case now being considered the necessary space-charge field has to develop in a time of the order of 2×10^{-5} sec., and thus the externally applied voltage must be higher.

There appear to be no experimental data with which to compare the above calculations, as the effect of initial photo-electric current on the time-lag of sparking seems to have been studied only in the case of over-volted gaps (13), where the time-lag is governed by the speed of electrons.

§ 4. COMPARISON BETWEEN THEORY AND EXPERIMENT

It has already been pointed out that, as far as the writer is aware, all experiments on the lowering of sparking potential for i_0 greater than about 10^{-12} amps. have been performed with a source of illumination in the form of an auxiliary spark-gap. Thus the actual magnitude of i_0 is not certainly known even as regards order of magnitude. Furthermore, it also varies with time, and its duration may be only about 10^{-4} sec. Comparison between theory and experiment is then somewhat limited except as regards order of magnitude until measurements have been made of the lowering of sparking potential for steady values of i_0.

Recent measurements by Brinkman (2) for a gap which required 10 kilovolts for breakdown at N.T.P. gave a lowering of sparking potential as shown by the curve of figure 4. A curve of similar form was also obtained by White (1). There is little point in making a direct comparison between these curves and that given in figure 1, principally because of the reasons already stated, but also because the gap length is different. However, it will be noted that the lowering begins to be observed in the region of values of i_0 predicted by theory. Further, it will be observed that the experimentally determined lowering of sparking potential for any particular value of i_0 is less than that calculated for the steady-state conditions, while it is greater than that determined in the preceding section on the 2×10^{-5} time-lag basis. This is to be expected in view of the fact that the duration of the illuminating spark may be $\sim 10^{-4}$ sec.

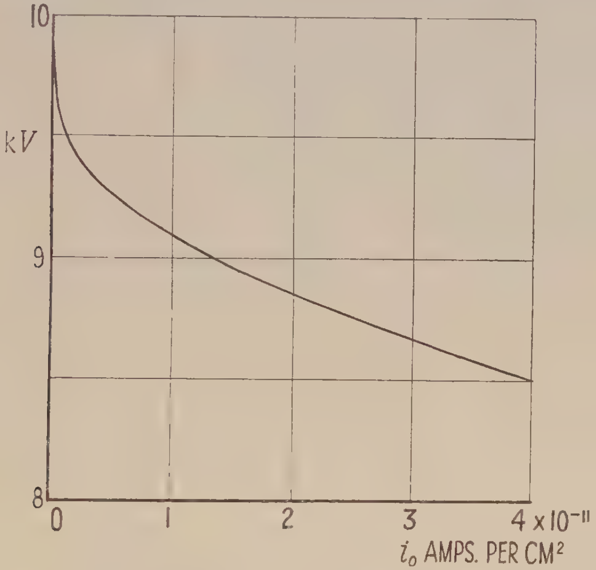

Figure 4. Curve derived from Brinkman's experimental results to show the variation of breakdown potential with photo-electric current.

ACKNOWLEDGEMENTS

The writer wishes to express his gratitude to Professor L. B. Loeb, who has been largely responsible for the development of the new theory of spark discharge and without whose suggestions and guidance the successful completion of the present work would not have been possible. The opportunity afforded by the Commonwealth Fund in the grant of a Fellowship is most gratefully acknowledged.

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DEMONSTRATIONS

A NEW MOUNTING FOR AN INDUSTRIAL GRATING SPECTROGRAPH.

Demonstrated 5 *April* 1940 *by* J. H. DOWELL, Messrs. Adam Hilger.

ONE of the disadvantages of the Eagle Mounting for a spectrograph for industrial use is the necessity for setting for focus, angle of grating and plate tilt for every setting for different wave-length ranges.

In the new mounting the grating and plate are connected by levers so arranged that the correct position of the plate and grating are controlled by the movement of a single lever, which is set to a scale indicating the wave-length range which will be included on the plate for any given setting.

The design follows that proposed by A. Cotton* and is very simple. The plate holder is pivoted on an axis passing through the centre of the slit, and has an arm connected to it of length equal to half the grating radius. This arm is connected to another lever of equal length which is attached to the grating mount, and, by means of a roller underneath, the mount is restrained to move on a line which passes through the centre of the slit, but by means of the lever can rotate on the axis of the roller.

If the plate is inclined at an angle to the centre line passing through the slit and the grating roller, the grating mount must also be inclined at the same angle, the levers being of equal length.

Also, since the grating is restrained by the roller to move in a line passing through the slit, correct focus and alignment will also be maintained.

The adjustment is performed in the spectrograph by another lever which enlarges the movement to a length suitable for an easily read scale engraved with the wave-length range inclined at any setting of the lever.

The variation of astigmatism depends upon the position chosen for the slit in relation to the plate, and in this spectrograph a position is selected which gives the minimum astigmatism towards the ultra-violet region.

For a full account of the spectrograph see the *Journal of Scientific Instruments* (1940).

THE PREPARATION AND PROPERTIES OF PHOTOCONDUCTING ALKALI HALIDE CRYSTALS, AND THEIR USE AS SPECTRAL FILTERS.

Demonstrated 28 *April* 1939 *by* W. R. S. GARTON, B.Sc., A.R.C.S., Imperial College of Science and Technology, London.

PHOTOCONDUCTIVITY is the property whereby certain substances exhibit a change of electrical resistivity upon illumination, and the class of such substances in which the attendant processes are best understood is that of the artificially produced alkali halide crystals. In these the phenomena are interpreted as a volume photoelectric effect, due to the temporary release by light of electrons previously bound in the crystal lattice; the electrons thus freed are supposed to migrate a certain average distance in an applied electric field. The considerable amount of experimental knowledge obtained, concerning the optical and electrical properties of the alkali halides, is due almost entirely to the work of Pohl (1) and his collaborators. On the interpretation of the observational material and on theoretical aspects, important contributions have been made by de Boer (2), and by Mott and Gurney (3), and valuable summaries are to be found in articles by Pohl (1) and by Hughes (4).

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* *C.R. Acad. Sci., Paris*, Jan. 1928.

The demonstration to which this account refers was considered to be justified by the striking nature of some of Pohl's experiments, and by a useful practical application to be described.

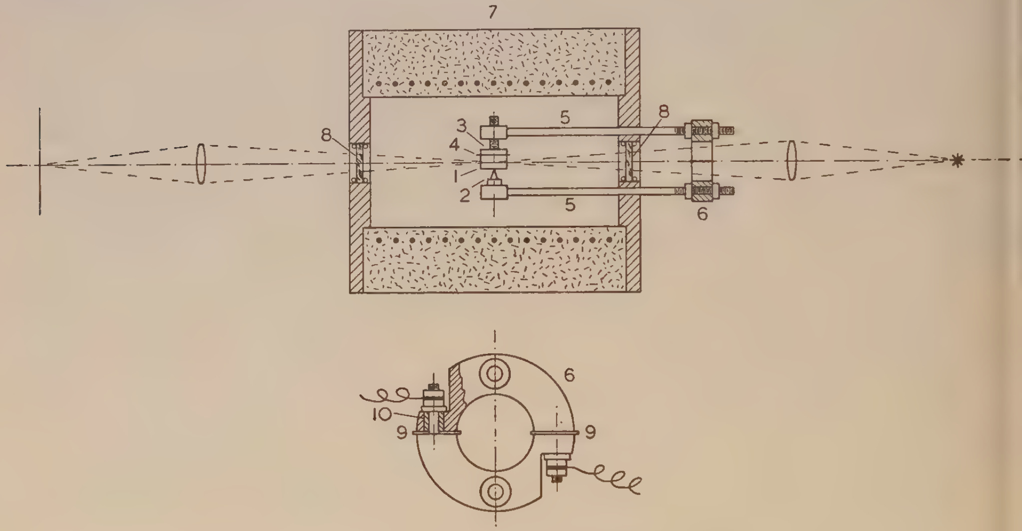

Figure 1. Apparatus for electron diffusion process.

A pure alkali halide crystal is transparent from far into the infra-red to a region in the ultra-violet varying from 1200 A. for LiF to 2300 A. for RbI. Treatment of the crystal by one of several methods results in the appearance of an absorption band, the position of which is a function of the lattice spacing only; the absorption maximum is shifted to longer wavelengths with increasing atomic number of alkali or halogen. In most cases this so-called "F band"* lies in the visible region, and so results in a coloration of the crystal, e.g. KCl becomes violet, NaCl yellow. The most striking of the methods of producing F-centres is that known as "electron diffusion" (5). The apparatus necessary is represented in figure 1. A clear crystal 1 is clamped between a pointed cathode 2 and a plane anode 3; steel rods 5 support the electrodes within an electric furnace 7. The rods 5 are held in position by a brass clamp 6, cut into halves which are bolted together, and insulated from each other by asbestos washers 9 and Pyrex sleeves 10. The electrodes may be of nickel, and it is advisable to insert a piece of platinum foil 4 between crystal and anode. Windows 8 and an aperture in the clamp 6 enable an image of the crystal to be projected upon a screen. The crystal is heated to within 200° c. of its melting point and a potential of about 800 volts is applied. On account of the shape of the cathode an intense electric field is produced in its neighbourhood, and electrons are able to pass into the crystal; the rate of entry is governed by the electrolytic displacement of a surplus of halogen$^-$ ions over metal$^+$ ions. Electrons during their passage become temporarily bound at certain lattice spots, the binding energy being of such a magnitude that the crystal will absorb light in a limited spectral range. As a result a coloured cloud is seen to grow from the cathode point, and gradually to fill the whole crystal. The opacity of this cloud in a crystal but a few mm. in thickness is very striking. A specimen of KCl treated in this way appears a deep violet to transmitted light, and the coloration is quite stable when the crystal is removed from the furnace and allowed to cool. If the field between the electrodes is reversed, the added electrons migrate, no supplementation occurs, and the coloured cloud disappears into the cathode point.

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* The name "Farbenzentren", or "F centres", is given to the active centres responsible for the absorption.

An untreated crystal shows no photoconductivity when exposed to visible or ultra-violet radiation. A coloured crystal, however, becomes photoconducting when irradiated by light falling within the F band, and a photocurrent of 10^{-9} amp. is easily obtained. The nature of the effects observed may be demonstrated conveniently by the use of an electrometer triode. Platinum wire electrodes, fused into the crystal, are connected in series with a battery of 30–100 volts and a high resistance leak of about 10^{10} ohms, and the variations of potential across the latter are applied to the grid of the triode. A suitable circuit may be found in the publication in which the valve is described (6); a critically damped galvanometer should be inserted in the anode circuit. With apparatus of this kind various experiments may be demonstrated which illustrate the photoelectric properties of the crystals. Suggestions as to suitable experiments readily appear from a perusal of the works cited.

Practical use may be made of the property of selective absorption possessed by crystals containing F centres, in their employment as spectral filters which transmit the whole or part of the ultraviolet, but absorb strongly in the visible region. The devices hitherto used for such a purpose, e.g. Wood's glass, have very limited ranges of transmission; where ultraviolet radiation outside those ranges has been required, free from longer wavelengths, there has been no alternative to the use of a quartz monochromator. The employment of an instrument of the latter kind involves a loss of light which is often serious enough to render work difficult or impossible, e.g. in photochemistry and ultraviolet microscopy. In such cases efficient ultra-violet filters are likely to be of use.

Figure 2 illustrates the spectral transmission of a KCl crystal of 3 mm. thickness, coloured by electron diffusion. Exposure (*a*) shows the spectrum of an "Osira" mercury discharge lamp with its glass envelope removed, and exposure (*b*) the same source with the KCl filter interposed; the horizontal streaks are due to the crystal being unpolished. It will be seen that such a filter cuts out all the visible radiation, except the far violet, and transmits the ultra-violet as far as 2350 A. Combination of an NaCl filter with one of KCl will remove the violet if its presence is undesirable. The KCl filters appear to retain their properties indefinitely, and are easily prepared by the method described; NaCl has a tendency to change from yellow to blue owing to colloidal aggregation, and it is more difficult to obtain good specimens. Further, for the preparation of filters, the electron-diffusion process is unreliable in the matter of reproducibility. It would appear from the literature that, for these reasons, a more satisfactory method of treatment is that known as "additive colouring", in which the heated crystal is exposed for a time to alkali metal vapour and then quickly quenched.

Figures for the F-band absorption coefficient and its variation with concentration of F centres * and with wavelength have been given by Mollwo(7). These data render possible an approximate calculation of the percentage transmission of a crystal of given thickness, at a particular wavelength. For example, coloured KCl has its absorption maximum at 5630 A., at which point the absorption coefficient of a crystal coloured densely by the additive process is of the order of 10 mm^{-1} Hence the percentage transmission of a crystal 3 mm. in thickness is at this wavelength about $100\,e^{-30}$; at 6400 A., and again at 4700 A., the value is $100\,e^{-4{\cdot}5}$, i.e. nearly 1 per cent. It follows that a KCl filter properly chosen will transmit no more than 1 per cent of radiation of a wavelength lying between these limits.

A study of the data mentioned suggests other useful possibilities, and it seems likely that a whole range of ultraviolet filters may be available. Thus, for instance, the position of the F band of LiF, with its maximum at 2500 A., suggests that an LiF filter could be used to transmit part of the Schumann region free of much of the ordinary ultraviolet, e.g. to transmit the mercury line 1849 A. free of 2537 A. These possibilities and others remain to be tested.

For the method of production of synthetic crystal specimens from the fused salts, reference may be made to a paper by Kyropoulos(8). The method described is probably the simplest of those used, and, provided reasonable care is taken as to purity, large crystals of sufficient optical quality for use as filters may be prepared.

The author's grateful thanks are due to Professor R. W. Pohl for the generous gift of a number of excellent crystals, and to Dr. C. C. Paterson and the Directors of the General Electric Co., Ltd., for the loan of an "Osira" lamp and accessories necessary for the projection of its ultra-violet spectrum.

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* When the "additive" method is used, this concentration is proportional to the density of the metal vapour.

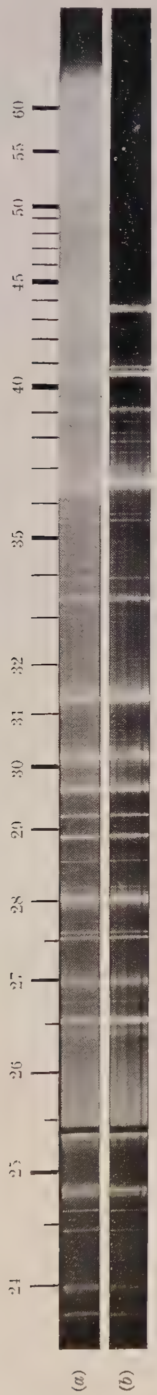

Figure 2. (*a*) Spectrum of "Osira" mercury discharge lamp with its glass envelope removed; (*b*) spectrum of the same source with a KCl filter interposed (KCl crystal 3 mm. thick coloured by electron diffusion).

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REVIEWS OF BOOKS

Advanced Algebra. by S. Barnard and J. M. Child. Pp x+280. (London: Macmillan & Co., Ltd., 1939.) 16*s.*

Users of Barnard and Child's *Higher Algebra* (1936, 585 pp.) may recall an unusual type of forward reference in the course of a proof of the binomial theorem (p. 341, last two lines): " . . . it will be shewn *in another volume* that $f(n)$ is a continuous function of x . . ." The reference is manifestly to the second volume announced in the preface, under the title of *Advanced Algebra*, which has now appeared. Some admiring surprise is legitimate, for, with most working mathematicians, such assertions are rash in the extreme. But it seems that a state of industrious retirement is immune from the incalculable laws of change, and that a collaboration started in the early 1900s has an almost infinite survival value.

A natural approach to the new volume is to follow up the point left in suspense three years before. The threads are readily picked up from the two-page index, with a little ingenuity, to avoid the false clue, "Binomial theorem, continuity of sum, 72". The required property is found in an unobtrusive position on p. 69 (Chap. IV). It is based on a deep and (for students of "H.A." grade) difficult theorem given 7 pages earlier,—Abels's theorem on the limit of $\sum_0^\infty a_n x^n$ as $x \to 1$. It is therefore particularly unfortunate that the proof of this theorem (p. 63) is incorrect. A most unlucky pendant occurs overleaf (p. 70): the advanced theorem on "convergence in an angle", whose inclusion (without proof) would have been a bold and almost laudable innovation in a book of this standard, is defaced by an over-simple and faulty argument, a vital condition (" entirely within ") being overlooked in a previous theorem.

These are certainly the worst mistakes of detail in the book, but they speak for what is in fact true: this is not the book for Honours students at a modern University outlined in the authors' statement: " Its scope has been determined by what is necessary for Honours degrees at the Universities ", which they qualify only by excusing themselves from including " such parts of Advanced Algebra as Matrices, Sets of Points, etc. . . . " This mention of Sets of Points (etc.) makes one wonder what topics of Pure Mathematics are regarded as *not* included under the heading "Algebra ", apart from " Geometry ", which is expressly distinguished further on in the Preface.

But it would be unkind to take the authors at their word. There is much more conclusive evidence in numbers. " H.A.", designed for the pre-University stage, had 585 pages; are 256 now to cover the " Honours " syllabus? That is all that remains of the new volume after cutting out Chapter IX, reprinted verbatim from H.A. (last chapter). (Why?)

In point of fact, the new book is a series of appendices to " Higher Algebra ", and is devoted chiefly to genuine algebra topics: Theory of Equations, Algebraic Geometry, and Number theory (Chapters II, VII, IX–XVII, and most of I). The acknowledged active contribution of Dr. G. T. Bennett obviously belongs to this field.

This major part, which I am not competent to judge single-handed as a teacher, seems from more expert evidence to be altogether praiseworthy. The treatment of invariants and covariants in Chapter XVIII is particularly commended as a very neat synopsis of matter hitherto dispersed, or deeply embedded. A certain geometrical bias in the presentation of algebraic material may surely be condoned for the sake of the rare mind likely to profit by it, since the book as a whole is clearly not for self-teaching, but will always need additional guidance from an enlightened tutor.

On the other hand, it grates on the analytical mind when (in Chapter I) the ordinary homographic transformation of the complex plane,—which knows only one point at infinity,—is placed in juxtaposition to the geometry of imaginary lines and the circular point at infinity. All that can be said is that genuine complex-function theory, in spite of the ambitious flights recorded above, takes such a back seat in the scheme that it is evidently not entitled to special consideration. The chief aim of Chapter V, on " The Complex Variable ", is the fundamental theorem of algebra and the bare minimum basis for the binomial theorem and other elementary expansions in Chapter VI. It is so sketchy that we find the theorem on the variation of a polynomial apparently applied to a function with a pole, and the remarkably elliptic proof " conversely, we infer " thus commented on in footnote : " If the student is not satisfied with this argument, he is referred to Hardy's *Pure Mathematics*, 4th ed. p. 439 ".

" Double Series " in Chapter III and " Uniform Convergence " in Chapter IV seem adequately treated in theory, and the faulty proofs mentioned, in Chapter IV, which are implicitly breaches of uniform convergence rules, would actually constitute good subjects for criticism as an exercise for the students. On this account it may be well to indicate the flaw on p. 63 here, for the benefit of users of the book. It is required to prove that, for

$$t_n = \sum_{r=1}^{n} a_r(1-x^r)$$

$$\lim_{x\to 1}\lim_{n\to\infty} t_n = 0.$$

The onus is transferred from t_n to $(1-x^n)$ by an inequality

$$(1-x^n)l < t_n < (1-x^n)h,$$

where l and h are numbers $\neq 0$ between which $\sum\limits_{n=1}^{\infty} a_n$ lies. But

$$\lim_{x\to 1}\lim_{n\to\infty}(1-x^n)\neq 0.$$

A turning movement is attempted through the (zero) limit of $(1-x^n)$ for $x=x_n=1-k/n^2$, k being fixed and n tending to ∞. But this can only give

$$\lim_{n\to 1}\lim_{x\to 1}(1-x^n)=0,$$

which is useless. (In fact, the onus should be transferred not to $(1-x^n)$, but to l and h, after taking the precaution to make $\sum\limits_{1}^{\infty} a_n$ zero, so that l and h can be chosen as near 0 as we please.)

Nothing has been said of Chapter VIII. It is a sequel (of 11 pages) to the elementary account of Probability in H.A., and seems framed so as to give only the simplest further facts required for the practical use of enumerative probability in finance, on the old-fashioned model.

As regards the general lay-out of the book, it is fairly easy to use. The detailed table of contents, index and cross-references in the body of the text show a care that is too often lacking in more important modern treatises. There is a collection of over 450 examples in the text and at the ends of chapters. The numbering for these latter sets, separately from the chapters, is confusing. The numbering of sections is started afresh in each chapter, and should therefore have been supported by indicating the chapter number at the top of the page. Small print should be reserved for matter that can be skipped on a general survey; here it often contains essential material for later proofs. Sources are only indicated generally in the preface, and are all old books. R. C. H. Y.

Fundamentals of Electricity and Magnetism, 2nd edition, by LEONARD B. LOEB. Pp. xxiv+554, with 223 figures. (New York: John Wiley and Sons; London: Chapman and Hall, 1938.) 24*s*. net.

This is an astonishing book. Dedicated to the engineering students of the University of California, it is written primarily for the benefit of students whose course in physics is covered in 26 one-hour demonstration lectures extending over two terms in their second year. Examining the table of contents of this work of imposing size, the only exceptional points that attract attention are perhaps the inclusion of a chapter on the e.m. and e.s. systems of units and Maxwell's equations (Ch. XXVI), and the final chapter on the thermionic and photoelectric effects. In reading the text, however, one is constantly impressed with the daring and refreshingly original, yet sound and logical, style which has been adopted. The preface intimates that the course given by the author to his engineering students deals with a fundamental knowledge of working principles, with relatively little material of a technical engineering nature. This hardly prepares one for the virile incursions into modern physics which liberally intersperse the text. To take a few examples. The chapter headed " Magnetic Properties of Materials " includes a description, with quantitative theoretical treatment, of the Stern-Gerlach experiment on atomic beams in a magnetic field, and discussions of the gyromagnetic ratio, the discrepancy between the Bohr and Weiss magnetons, and the moment of the spinning electron. Chapter XXVI includes a full derivation of Maxwell's field equations, the wave equations and their solution. The chapter on static electricity gives the application of Debye's dipole theory to show the dependence of the dielectric constant on temperature. In the portion of the final chapter relating to thermionic emission, four forms of equation connecting emission with temperature are given and discussed, and attention is directed to the Sommerfeld-Pauli conception of free electrons in metals and to the Fermi-Dirac statistics.

At the end of the book considerable space (75 pages) is devoted to problems, for which numerical solutions and, here and there, comments on the subject-matter are included. The selection ranges from simple exercises on the forces between magnetic poles to calculations of the forces between α-particles and atomic nuclei, on the theory of the cyclotron, and a final one on a series of radio-active disintegrations.

An unusual proportion of space is devoted to expositions of the historical development of the subject.

All this makes an unusual and unconventional, but undoubtedly stimulating and entertaining book. It may well repay the attention of the enterprising student of physics as well as of the engineering student. The dedication to the latter is indeed a fine compliment. D. O.

Statistical Thermodynamics, by R. H. FOWLER and E. A. GUGGENHEIM. Pp. x+693. (Cambridge: The University Press, 1939.) 40*s*. net.

Until comparatively recently statistical mechanics was a subject which each worker had to pick up as best he could; Gibbs's book was the only one available, and was far from helpful to any but a few specialists. Even much more recently the only connected accounts were those of Rice (rather elementary), Tolman (somewhat chemical) and of R. H. Fowler (extremely difficult), together with chapters or groups of chapters in books on other subjects. Each of these is still useful in its own field, but the choice has been greatly widened by the issue of Tolman's new book, which discusses the foundations of the theory very thoroughly, if not rigorously, and two books which set out the applications. Of these, one by Chapman and Gowling (reviewed in this volume, p. 273) deals with transport phenomena, and the other, now under review, restricts its attention in the main to equilibrium phenomena.

Statistical Thermodynamics makes no claim to probe deeply into the foundations of the subject, though it gives arguments, adequate for the physicist, why statistical methods may and should be adopted in so many problems. It does make a claim to be less severely mathematical than Fowler's book, and in a sense this is true ; there is less demand on the mathematical equipment of the reader, but by the nature of the subject the appeal to the logic underlying mathematical treatment is as frequent and demands as close attention as in the larger book.

The treatment takes the form of a gradual development of the theory and its applications, in the manner of a text-book, but without the benefits which accrue to the reader if exercises are set for him to work out. After the introductory chapters, in which temperature and entropy and the thermodynamic functions are introduced, the simplest systems—perfect gases and ideal crystals—are discussed in some detail. Then there is a chapter on chemical equilibrium and evaporation, in which the question of entropy values at absolute zero is discussed, and Nernst's theorem stated in the modern form as the principle of the unattainability of the absolute zero. The next chapter, a difficult one, makes the transition to the grand canonical ensemble, or rather to its quantum analogue.

Each of the remaining eight chapters contains an outline sketch of some subject of physical chemistry, from the point of view of statistical mechanics, and makes full use either of direct statistical methods or of thermodynamics, a justifiable procedure, since the thermodynamic formulae have been established in the introductory chapters. It is hardly necessary to mention that in this introduction, the various statistics—Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein—are all developed on an equal footing.

In the final eight chapters there is frequently an account of quite recent work, most notably in the one on imperfect gases, where a new method, only opened up in the last year or two, is included. The same up-to-date quality is present in the chapter on electrolytic solutions, where the work of Onsager and others is set in its correct perspective. It is difficult to find a simple account of the modern electron theory of metals which includes a convincing account of the Bloch theory and the Brillouin zones, and Chapter XI goes far to meeting this need for the non-metallurgist. The ubiquitous subject of order-disorder transformations in alloys is to be found in Chapter XIII, whilst the last chapter takes up a miscellaneous group of questions under the general title " Electric and magnetic properties ".

Although the book is arranged in systematic text-book fashion, it is doubtful whether many students will find that their crowded curricula leave them time to work right through it. Even so, a study of the first few chapters will give a sound understanding of the subject, and the whole book will in any case remain a standard work of reference for a long time. J. H. A.

Colour Cinematography, by Major ADRIAN BERNARD KLEIN. Pp. xxii + 463. (London: Chapman and Hall, Ltd., second edition, 1939.) 30*s*. net.

Major Klein's book is very comprehensive and must be an invaluable work of reference for anyone engaged in work on colour cinematography. A second edition (the first appeared in 1936) has now been published. We are told that the intervening period "has been remarkable for patent activity", and full lists of patent specifications are a feature of the book.

An appendix on filter calculations (by Mr. S. H. Groom) has been added, while in the preface to the second edition (and in another appendix) Major Klein gives his own views on the difficulties, failings and possibilities of the colour film. J. A. H.

Photography by Infrared, its principles and applications, by WALTER CLARK. Pp. x + 397. (London: Chapman and Hall, Ltd., 1939.) 25*s*. net.

Dr. Clark, in his preface, says that this book "is intended for the guidance of the practical infrared photographer, whether he is concerned with the commercial or artistic aspects of its subject or its applications in the scientific and technical fields". This intention has been successfully carried out, for there can be few problems likely to be encountered by the infra-red photographer on which he will not here find useful guidance. Each chapter is provided with a very full bibliography.

The different types of sensitive material available are set out, as are also the methods of sensitizing, while the applications of infra-red photography in aerial and survey work, medicine, metallurgy, the examination of documents and other materials are described. Sources of radiation are also considered, and data are given which enable exposures to be calculated for the infra-red photography of hot objects at different temperatures. There are also two chapters on "Photographic darkroom practice" and "Characteristics of photographic materials" which have an application considerably wider than is suggested by the title of the book, and which arouse the hope that perhaps Dr. Clark will follow this volume with a general photographic text-book. J. A. H.

General Physics, by F. C. CHAMPION. Pp. 157. (London: Blackie and Son, Ltd., 1939.) 4*s*. 6*d*.

This book, which is the first part of a complete course in physics, is intended for students taking First and Second Year Courses and is designed to prepare them for examinations such as the General B.Sc. of London University. In addition, the author states that by omitting certain sections the book caters for the needs of Intermediate students, these needs appearing to range from the theory of Hare's apparatus to that of the rotation viscometer, the compound pendulum and the bifilar suspension. It is a difficult task to produce a comparatively small volume which caters both for Intermediate and Final students.

The volume, after a general introduction, leads on from kinematics to the study of dynamics, statics, units, the acceleration due to gravity, gyroscopic motion, elasticity, hydrostatics, and the properties of gases, liquids at rest and fluids in motion. It concludes with a good collection of examples together with answers and hints for solution. The print and diagrams are both excellent and teachers of physics will find the book stimulating.

F. H. N.

Sparks, Lightning, Cosmic Rays: An Anecdotal History of Electricity, by DAYTON C. MILLER. Pp. xvii+192. (New York: The Macmillan Company, 1939.) 11*s*.

In the present times of stress it is good, indeed, to be able, momentarily, to relax. And what more unsophisticated and pleasant relaxation could we expect to have than in the reading of the "Christmas week lectures for young people" given by Professor Miller at the Franklin Institute in 1937? The expectation is amply realised in the reading of this charming book. For 1938, meetings in honour of Benjamin Franklin had been arranged by the Franklin Institute, and it was therefore considered appropriate that the children's Christmas lectures in 1937 should give an account of the history of electricity, with particular reference to the scientific investigations of Franklin in that field.

The book consists of three lectures, and their subject-matter leads one to suspect that they had as wide an appeal to an audience of "children" of all ages as do our own Christmas lectures at the Royal Institution! The first lecture is on "sparks" and takes us from the experiments of Thales and William Gilbert to the electrostatic generator of Van de Graaff. The second lecture, on "lightning", deals mainly with the life of Franklin and his own contributions to our understanding of the nature of electricity. And in the reading of this lecture one cannot help but be impressed by the versatile genius of Benjamin Franklin. Printer, scientist, public administrator and statesman; in each rôle Franklin had a special contribution to make for the benefit of the society in which he lived; but which society he regarded with no greater respect than, perchance, it deserved. Thus in 1782 he wrote from Paris, where he represented his country for nine years, to Joseph Priestley "that he would rejoice if he could recover the leisure to search 'into the works of nature; I mean *inanimate*, not the *animate* or moral part of them; the more I discovered of the former the more I admired them; the more of the latter, the more I am disgusted with them. Men I find to be a sort of beings very badly constructed, as they are generally more easily provoked than reconciled, and more disposed to do mischief to each other than make reparation . . . I have been apt to think that there has never been, nor ever will be, any such thing as a *good* war, or a *bad* peace'". Times may have changed; but human nature, seemingly, not at all. And should it be said that Franklin was ahead of his times, or would it be more true to accredit a lack of imagination to modern statesmen, when we read that Franklin "discussed plans for a general peace in Europe; he thought it might be possible to persuade the various sovereigns to send delegates to one place. 'I think they might agree upon an alliance against all aggressors, and agree to refer all disputes between each other to some third person, or set of men or power. Other nations seeing the advantage of this, would gradually accede; and perhaps in one hundred and fifty or two hundred years (in 1933 or 1983), all Europe would be included.'"? One day, perhaps, this dream may be fulfilled, but not before that animate or moral part of nature has learnt something of that humility with which Franklin, in no small measure, seems to have been imbued. Thus he writes, "I find a frank acknowledgement of one's ignorance is, not only the easiest way to get rid of a difficulty, but the likeliest way to obtain information, and therefore I practice it. I think it an honest policy. Those who affect to know everything, and so undertake to explain everything, often remain ignorant of many things that others could and would instruct them in, if they appeared less conceited". In this lecture Professor Miller also corrects two "popular" beliefs. The first, that Franklin, in 1755, and not Faraday, showed that the charge on a hollow conductor resided wholly on the outside surface; the second, that

Priestley, in 1766, and not Coulomb, proposed the inverse square law. There is also given an account of Franklin's experiments with lightning, of his introduction of lightning conductors, and of such other diverse accomplishments as the development of his " armonica " and his use of bifocal spectacles.

The scope of the last lecture is wider than its title of " cosmic rays " would suggest. The subjects treated in this lecture are diverse and include the discharge of electricity through gases, wireless, the aurora polaris, cathode rays, radioactivity, ascents into the stratosphere, science and the world war, and, finally, cosmic rays themselves.

For young people, in their latter teens, this book should provide most excellent reading and, for those who are not so young, a few pleasant hours of refreshment and rejuvenation.

W. B. M.

The Raman Effect and its Chemical Applications, by JAMES H. HIBBEN. Pp. 544. (New York : The Reinhold Publishing Company ; London : Chapman and Hall, Ltd., 1939.) 66*s*. net.

Sir William Bragg once pointed out in the course of a lecture that every so often the study of a physical phenomenon has developed into a branch of science and then been sloughed off. This seems to be happening now in the Raman effect. From its discovery in 1928 it has grown dramatically, so that it is now possible for a book, with 2,000 references at the back, to be devoted to it.

The effect is of particular interest to the structural chemist, for the appearance or non-appearance of certain lines in the Raman spectrum of a substance is a guide to the symmetry of the molecule, while the numerical magnitudes of the vibrational frequencies deduced from the displacements of the exciting line help in determining force-constants. A likely model having a certain symmetry is assumed for the molecule, and from this model may be deduced the lines to be expected in the Raman effect, their states of polarisation, and rough estimates may be made of their frequencies and relative intensities. This expectation can then be compared with the observed spectra; if there is disagreement then a fresh model must be tried. The information yielded by the effect is complementary to that given by infra-red spectra.

This is the first book written in English to be devoted solely to the Raman effect. It is strongly recommended to workers on the subject, and it will be found useful to students of chemistry. Part I consists of a general discussion of the technique and theory of the effect. The portion devoted to technique is the least satisfying in the book. In the next edition this part should be re-written ; meanwhile those who find it too brief will be helped by the copious references. The remainder of this part, which deals with the theory of the effect, was written in collaboration with Edward Teller. This exposition is excellent; it is clear, direct, and couched in simple terms. Part II is a study of the results so far obtained for organic substances, and Part III is a similar study of inorganic substances. The organic substances are considered first, since they lend themselves better to a systematic treatment. Separate chapters are devoted to aliphatic hydrocarbons, alcohols, ethers, and so on. This part occupies nearly 200 pages, and the inorganic part is nearly as long. Both parts are extremely useful compilations; as well as containing much data in a handy form, they are packed with provocative opinions, most stimulating to the reader.

The bibliography and indexing are particularly useful; there is a bibliography of about 2,000 references, an index of substances, and an index giving places in the text where the separate references are quoted. The appearance of the book follows the normal practice of the Chemical Catalog Company, to which the Reinhold Corporation is the successor. The least satisfactory feature of the book is its price. A. C. M.

Mr. Tompkins in Wonderland, by G. GAMOW. Pp. x+91. (Cambridge: The University Press, 1939.) 7*s*. 6*d*.

This is a most delightful fantasy in which the hero, Mr. Tompkins, is transported in a series of dreams to other universes in which the fundamental physical constants have very different values from those observed in terrestrial laboratories. By intensifying gravitational attraction a million times, by slowing up the speed of light to one ten-millionth, and by supercharging Planck's constant to the value of one erg-second, Professor Gamow has created wonderful new worlds in which the mysteries of modern physics are visible to the naked eye. The expansion of the universe is accelerated and its dimensions reduced until Mr. Tompkins can live through a cycle of pulsation in two hours. The uncertainty in the position of a billiard ball is magnified until billiards becomes hydrodynamics. The perpetual youth of commercial travellers—but it would be grossly unfair to the author to reveal any more of his secrets and surprises.

This is the first book which makes the principles of quantum theory and relativity not merely intelligible, but familiar, obvious and almost platitudinous. It is perhaps sufficient to say that it will satisfy the critical eye of Einstein and Planck, and would have delighted the whimsy of Lewis Carroll. G. T.

Mechanics Applied to Vibrations and Balancing, by D. LAUGHARNE THORNTON. Pp. xii+529. (London: Chapman and Hall, Ltd., 1939.) 36*s*. net.

The object of this treatise is to give an account of the general theory of vibrations and its applications to problems of physics and engineering. The very wide field which is covered by the author is indicated by the following list of topics, which is by no means exhaustive:—balancing of engines and locomotives, wave propagation in elastic materials, vibrations of beams, plates and membranes and vibrations of rotating shafts and discs. These topics are treated in considerable detail, and in addition the value of the book is enhanced by the frequent numerical examples and the excellent diagrams. This book is undoubtedly a substantial addition to the literature on vibration theory, and the following detailed criticisms do not detract from its general value and importance as a work of reference.

The statement of the conditions for the balancing of excentric masses on a shaft (page 9, equations 3.1 and 3.2) is misleading and erroneous, for the conditions are vectorial in character. This is implicated, to use a favourite phrase of the author, in the accompanying examples, but should have been clearly and explicitly. In the discussion of the cubic equation, $\lambda^3+p_1\lambda^2+p_2\lambda+p_3=0$, (page 71) we find the remarkable statement that $p_1 p_2 > p_3$ is the condition for two roots "to be negative or imaginary with one real part"! It is a pity that this result, so fundamental in the theory of governors, is not proved, stated correctly and extended to quartic equations. Another remarkable omission from this book is a general discussion of the production of instability in systems of two or three degrees of freedom by linear damping forces. There are brief references to flutter theory but no theoretical discussion of this major problem in aircraft construction.

Fourier series are extensively used throughout the book but there is no discussion of their convergence, or, what is more important for the practical man, the *rapidity* of their convergence in relation to the continuity of the generating function. On the other hand the author gives a discussion of Riemann's method of integrating hyperbolic equations, of Hamilton's canonical equations and of the Principle of Least Action—subjects interesting in themselves but scarcely of importance for technical applications.

It is curious also that, although the exposition of Riemann's method occupies pages 314–318, his name does not appear in the index. But neither do the names of Dalby, the great authority on engine balancing, or of Den Hartog, the author of a well-known and important treatise on vibration theory! There is no reference to Timoshenko's book on the same subject, and no adequate reference to the standard work by Morris on vibrations of shafts and air-screws. These omissions, however, can easily be repaired in a second edition, which will then be one of the more important treatises on this subject.

G. T.

Theory of Probability, by H. Jeffreys. Pp. vi + 380. (Oxford: The Clarendon Press, 1939.) 21*s*.

The ideas of the author as put forward in his well-known *Scientific Inference* are now developed further in the book under review, which incorporates his more detailed researches published in numerous papers scattered over almost all the well-known journals of the physical sciences.

The scope of the book goes further than providing a philosophical basis of probability—in fact it is concerned with scientific inference from observational data in general. Its chief object is the bridging of what are said to be the controversial attitudes of the physicist and statistician. The physicist is said to claim that he can prove his hypothesis with the help of observations, which of course is a logical fallacy since there are always other hypotheses that may tally with the observed data. Opposed to this optimistic attitude of the physicist is that of the pessimistic statistician who confines himself to disproving (if he can) what is known as a null-hypothesis without ever reaching a decision as to which of the remaining alternatives is true. The appropriate method of scientific inference, the author says, lies in between these two extremes of complete acceptance and complete refusal, and it is the object of the theory to provide a quantitative measure for the truth of an hypothesis—in other words, the probability of the hypothesis.

The author's typical physicist and statistician would appear to be rather dogmatic. Modern physicists, are, of course, quite aware that they cannot prove a theory and that there are often other ways of explaining observed facts; as an example, one need only quote the "wave" and "corpuscle" model of modern quantum theory. Indeed, there is a conception in modern physics often referred to as "the simplest theory" which is generally accepted as the truth for the time being, i.e. until it has to be modified in accordance with new observations. Jeffreys has now set out to give scientific precision based on the appropriate language of probability to this commonsense notion of "simplest".

On the other hand the statistician has recently extended the scope of his methods beyond the mere disproving of negative null-hypotheses. E. S. Pearson's notion of the probability of admissible alternatives and his "power function" are certainly steps in this direction, although they differ in detail from what Jeffreys has developed.

The fundamental notions of the author's theory are based on "rules suggested by the procedure of logicians and pure mathematicians" (pages 8–10). These are kept in general terms, and it is impossible to disagree with these rules, which, as the author says, may be considered to be platitudes. The difficulty (and danger) lies in their interpretation. To give an example, nobody would object to rule 3: "Any rule given must be applicable in practice. A definition is useless unless the thing defined can be recognised in terms of the definition when it occurs. The existence of a thing or the estimate of a quantity must not involve an impossible experiment". But Jeffreys concludes that we must rule out " in the first place, any definition of probability that attempts to define probability in terms of infinite sets of possible observations, for we cannot in practice make an infinite number of observations. The Venn limit, the hypothetical infinite population of Fisher, and the ensemble of Willard Gibbs are useless to us by rule 3". Here it may be remarked that all that is required for defining an " infinite population " is the notion of a mathematical limit, as the number of observations is increased indefinitely. This, as is well known, may clearly be defined as a relationsip holding for *finite* numbers of observations. Admittedly there are physical occurrences (such as the number of earthquakes observed) which are known to be smaller in number than a well-established upper limit, and it may be well worth while to modify the conception of an " infinite population " when dealing with such occurrences, but this does not justify the unconditioned refuting of a theory which has proved most useful in many other cases.

From another of his fundamental rules (rule 5) the author concludes " no objective definition of probability in terms of actual or possible observations, or possible properties of the world is admissible ". He thus opposes the opinion of von Mises and others who have made an attempt to treat probability as a natural science. The point at issue has given rise to controversy in recent years ; in spite of the shortcomings of von Mises' conception of a " collective ", there is, in the opinion of the reviewer, no justification for making the opposition to von Mises' ideas a " fundamental rule ".

Now to the details of the theory. Its most striking feature is a qualified return to Bayes' conception of *à priori* probability, which had almost been eliminated from recent researches in biological statistics carried out by R. A. Fisher and his school. But it appears that the difference in opinion is explained by the different requirements of the physicist as compared with those of the biologist.

It is remarkable, however, that although setting out from notions which are fundamentally different from those usually accepted, the author reaches results which are very similar to those obtained by modern methods such as the $\chi^2 t$ and z-tests. He replaces these tests by his statistic K, which appears in various forms according to the problem, and the significance of which may be judged with the help of appended tables.

A number of interesting applications appear as examples ; of particular interest is the determination of the epicentre of a shallow earthquake by the method of least squares. The student who is interested in the more advanced aspects of this theory, which the author has developed in a number of his recent publications, is advised to study the relevant passages in this book first. Generally, however, the value of this book lies mainly in the novelty of its ideas. It may be regarded as stimulating reading for the research worker rather than as a standard text-book to be used by the student. H. O. H.

The Physical Examination of Metals, by BRUCE CHALMERS. Vol. I. *Optical Methods*. Pp. viii + 181. (London: Edwin Arnold, 1939.) 14*s*.

This is a very interesting book, though not quite what one might have expected from the title. It is rather an introduction to the study of several sections of optics, illustrated by examples taken exclusively from metallurgical subjects. This is not intended as adverse criticism; indeed in the hands of the author the method forms a good one for introducing the reader to some of the very recent advances in metallographic technique—advances in which the author has taken a prominent part.

After an introductory chapter discussing the general properties of light, the book deals with geometrical optics, and then passes on to interference problems. The author shows, amongst other uses of this property, how the thickness of electrodeposited films can be measured by interference methods. A chapter on diffraction is illustrated by its use in measuring particle size, and by a discussion on the resolving power of the microscope, while the final chapters deal with polarized light and sources of light.

In view of the probability that a second edition of this useful book will be required it may be worth while to point out a few slips that have escaped detection in the proofs.

On page 26 the Curie point of iron is given at 1040° C.; this surely should be 1040° K. On page 63, for Fig. 36 b we should read Fig. 37 b, and on page 102 we find "A second group . . . are."

Again, would it not be well to reverse either Fig. 1 or Fig. 2 so that the wavelength increased in the same direction in both ? It might also be advantageous to state the focal length of the mirror referred to on page 6, in view of the fact that the distances between it and the lamp and scale are specified, and finally, there is surely a mistake in Fig. 97. The ultra-violet focus should be shorter than that of the infra-red.

These are all minor points, and the book can be thoroughly recommended to all metallographers. J. L. H.

Matter, Motion and Electricity, a Modern Approach to General Physics, by HENRY DE WOLF SMYTH and CHARLES WILBUR UFFORD. Pp. xiii + 648 + 2 tables inside cover. (London: McGraw-Hill Publishing Company, Ltd., 1939.) 25*s*.

In their introduction the authors explain how this book grew over a period of years out of a special course of lectures given, as an introduction to more advanced physics, to undergraduates at Princeton who had already taken some elementary physics at school. The authors state that their purpose had been " to plan a course that reviewed fundamental principles sufficiently to ensure a solid base on which to build and yet avoided too exact a repetition of the conventional beginners' course ". And considering the enormity of their task they have achieved their purpose in no small measure and in a most refreshing manner. Thus already on page 5, we are shown cloud-chamber tracks of alpha-particles; the first chapter is on "Atoms and Molecules " and develops the atomic theory from considerations of elementary chemistry. This, to one whose early impressions of physics are gloomily associated with specific gravities and elastic moduli, seems a most pleasant method of approach and one which is calculated to give the student a desire to grapple at once with fundamentals.

In this book the m.k.s. system of units is used. For one whose mind is as irretrievably steeped in the vagaries of e.s.u. and e.m.u. as my own, this does tend to make for a certain feeling of anomaly. Thus it does seem a little unnatural for the force between two charges q_1 and q_2, separated by a distance d, to be equal to $q_1q_2/4\pi\epsilon d^2$ newtons, where ϵ is the dielectric constant; the dielectric constant for a vacuum is, as a result, equal to $1/4\pi \times 9 \times 10^9$ farad/m instead of unity. And since the book is intended for students who have already done some physics, and will also probably have done it in terms of e.s.u. and e.m.u., may it not also introduce a little confusion for them too ? However, if the m.k.s. is preferable to the c.g.s. system then a start must be made somewhere, and this book is in the nature of a crusade. And the question as to whether the m.k.s. system is really preferable to the c.g.s. system has been, and will be, critically discussed elsewhere; the discussion of such a question is beyond the scope of this review.

It is far easier to criticize than to write such a book, and it is therefore with the most extreme diffidence that I venture to make a few observations which may perhaps savour of criticism. Thus it seems a little strange to find, in Chap. xix, that in the description of the experiments for determining e/m and v for electrons there is no single mention of the name of J. J. Thomson, although the method described is that devised by him. In Chap. xii, however, in which the determination of the electronic charge is described, the name of Millikan is included thirty-one times. Perhaps this is merely symptomatic—an indication that modern nationalistic tendencies have crossed even the Atlantic! Similarly, in introducing the theory of molecular magnetism the names of Gilbert, "physician to Queen Elizabeth", and of Ampère are mentioned, but those of Weber and of Ewing not at all, while the Bohr theory is given as just a theory without an author; Bohr's name does appear in a problem at the end of this chapter, but it would still be difficult to associate him with his theory. While admittedly in any development of the subject of atomic physics it is unnecessary for a student to attach a name to a theory or to an experiment, it is, nevertheless, a pleasant custom which, quite apart from the sentimental aspect, does offer some practical advantage from the point of view of classification.

Other points may be briefly summarized. The statement that the experiment, in which carbon dioxide is sealed in a glass tube which is then warmed until the meniscus disappears, "could be performed with water if a glass tube that was strong enough to sustain the necessary pressure could be made" shows to what extent Callendar's last experiments on the properties of water near the critical point* are still, unfortunately, relatively unknown. The experiment described above, using water sealed in a quartz tube, however, constituted one of his lecture demonstrations. The statement that "the legal standard for measuring temperature is a hydrogen-gas thermometer" calls to mind comments made by a previous reviewer in this Journal.† In describing the electrostatic generator it is stated that "The great advantage of the device is that it builds up very high voltages". The following statement is then made in support of this claim: "For example, each of the two original generators constructed by Van de Graaff will build up a potential of some two hundred thousand volts, so that if we make one positive and one negative we get a difference of potential of about four hundred thousand volts." In the light of performance data published during the last few years a more conservative example could hardly have been given in support of the claim to the attainment of high voltages!

An interesting feature of the book is the treatment of the subject of magnetism. This follows the chapter on the action of one current on another and is treated simply as the interactions between moving charges. Another feature is that just sufficient mechanics has been included to make the subsequent treatment, with regard to the motion of particles, etc., perfectly clear. Alternating current theory, wave theory, isotopes and radioactivity have all been accorded very adequate treatment, and the book concludes with a comprehensive chapter on "Radiation and Matter". Throughout the book great care has been taken to present a logical development of the subject, and the authors have lost no opportunity of emphasizing those more philosophical considerations which may serve to weld the different parts into one consistent whole. In their preface the authors state that "This book is not intended for self-instruction. It needs to be supplemented with lecture demonstrations, explanations of problems" (of which are given some five hundred besides illustrative problems) " and descriptions of practical applications. It is primarily concerned with the principles of physics and the method by which they are discovered." For this purpose, as a textbook in general physics, and as an introduction to a wider course on atomic and nuclear physics, this book should be admirably suited. For those who use the m.k.s. system this book should be of great use, while to those who prefer to use the c.g.s. system it should still provide useful supplementary reading for first- and second-year students, since the development of the subject, and of the principles involved, can be followed and appreciated without undue attention being paid to the system of units. W. B. M.

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* Callendar, H. L., Howard Lectures, Royal Society of Arts, 1927, and *Proc. Roy. Soc.* A, **120**, 460 (1928).

† "E. G.", *Proc. Phys. Soc.* **51**, 1049 (1939).

The Theory and Practice of Electron Diffraction, by G. P. THOMSON and W. COCHRANE. Pp. xi+334. (London: Macmillan and Co., Ltd., 1939.) 18*s*.

It is a remarkable fact that although de Broglie's thesis on the wave-length to be associated with the electron was published in 1924, and Elsasser's suggestion that electron diffraction would give an experimental test of the theory was made in 1925, and even Schrödinger's equation and derivation of the energy levels in hydrogen, which placed the wave nature of the electron beyond reasonable doubt, appeared in 1926, it was not until 1927 that the famous experiments of Davisson and Germer and of Thomson were carried out. Moreover, it appears that the stimulus to these experiments was provided in the main not by the theory at all, but by a chance observation in the case of Davisson and Germer and by anomalous results on electron scattering in gases in the case of Thomson. At that time, probably, the attention paid by experimental workers to the most recent theory in physics was not so great as it became later during the heyday of the advance that followed the discovery of wave mechanics.

In spite of the fact that the formulation of Schrödinger's equation preceded the discovery of electron diffraction, it remains true that the phenomenon of electron diffraction provides the most direct experimental proof of the physical basis of this equation, of its interpretation and of the whole structure of modern theoretical physics which has been built up on it. Any development of quantum mechanics which attempts to base its axioms as closely as possible on experiment must start from the facts of electron diffraction. It is therefore satisfactory to find in the book under review a full account of the early experiments and of later ones designed to test the validity of de Broglie's formula for the wave-length, and also some discussion of their interpretation. The intensity of the scattering is also discussed; here our only criticism is that no mention is made of the information about the intensities that has been obtained through the scattering of electrons by the inert gases.

However, the main interest in electron diffraction has long ago shifted away from the support that it gives to wave mechanics, and now lies in its usefulness as a tool for the investigation of the structure of surfaces, and to a lesser degree of gas molecules. Electrons differ from X rays in being much more heavily scattered by the individual atom, and are therefore suitable for the investigation of very small conglomerates, such as individual molecules or small crystals projecting from a surface. Much of the book under review is devoted to the consideration of surface problems, for which the method is now yielding valuable results. There are chapters on the growth of crystals, on the structure of oxide films on metals, on the polished layer and on lubricating oils. There is also a chapter on gas molecules, one on the measurement of inner potentials in crystals, and one on electron polarization. Altogether it is most satisfactory that so excellent an account of the subject, and particularly of the researches of Thomson's own school, should have appeared before so much research was interrupted by the present emergency. N. F. M.

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